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# Mechanistic and exploratory organic photochemistry and the synthesis of strained cyclic cumulenes

Mary Morgan Kirchhoff  
*University of New Hampshire, Durham*

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**Mechanistic and exploratory organic photochemistry and the  
synthesis of strained cyclic cumulenes**

**Kirchhoff, Mary Morgan, Ph.D.**

**University of New Hampshire, 1992**

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**MECHANISTIC AND EXPLORATORY ORGANIC PHOTOCHEMISTRY  
AND  
THE SYNTHESIS OF STRAINED CYCLIC CUMULENES**

**BY**

**MARY MORGAN KIRCHHOFF  
B.A. RUSSELL SAGE COLLEGE, 1977  
M.S. DUQUESNE UNIVERSITY, 1982**

**DISSERTATION**

**Submitted to the University of New Hampshire  
in Partial Fulfillment of  
the Requirements for the Degree of**

**Doctor of Philosophy**

**in**

**Chemistry**

**December 1992**

This dissertation has been examined and approved.

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December 2, 1992  
Date

## **DEDICATION**

**To my husband,**

**Steve**

**my children,**

**Sean, Jim, Jackie, and Jennie**

**and my Mom and Dad,**

**Jim and Joan Morgan**

## **ACKNOWLEDGMENTS**

Many people have been instrumental in helping me complete this degree. I would like to thank my research advisor, Dr. Richard P. Johnson, for his ideas, guidance, and understanding during the last five years. Thanks to the rest of my committee, Dr. Ken Andersen, Dr. Chris Bauer, Dr. Anita Klein, and Dr. Gary Weisman, for their suggestions regarding my dissertation. A big thank you to Dr. Howard Mayne, for getting me through P-Chem on the first try (a class I didn't want to repeat). Thanks, too, to Dr. Gary Weisman, for being such a great instructor, and providing me with a model for my own teaching.

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## **ABSTRACT**

### **MECHANISTIC AND EXPLORATORY ORGANIC PHOTOCHEMISTRY AND THE SYNTHESIS OF STRAINED CYCLIC CUMULENES**

by

**MARY MORGAN KIRCHHOFF**

University of New Hampshire, December 1992

The photoaddition of 1,2-cyclononadiene to naphthalene gives para adducts as the primary products, accompanied by a minor amount of the meta cycloadduct. Photolysis of naphthalene and 1,2-nonadiene did not yield any addition products, nor did irradiation of anthracene and 1,2-cyclononadiene, indicating that the reaction is sensitive to the structure of both the allene and arene.

Dichlorocarbene can be cleanly generated photochemically by irradiation of 7,7-dichlorodibenzo[a;c]bicyclo[4.1.0]heptane. This new method of producing dichlorocarbene permitted the first measurement of the absolute rate constants for the addition of dichlorocarbene to a series of olefins. Additional studies on this carbene included irradiation of the precursor with benzophenone, a triplet sensitizer. This protocol, however, did not lead to formation

of triplet dichlorocarbene. The carbene was found to insert into the methine bond of 2-methylpentane, but no insertion products were detected with cyclohexane. The dichlorocarbene precursor was subsequently modified, yielding potential progenitors to chlorocarbene, benzylchlorocarbene, and chloromethylcarbene.

1,2,3-Cyclooctatriene was generated through fluoride-induced elimination of 2-chloro-3-trimethylsilyl-1,3-cyclooctadiene. The highly reactive butatriene was trapped as its 1,3-diphenylisobenzofuran adduct. Synthesis of the eight-membered ring completes the C<sub>6</sub>-C<sub>10</sub> series of cyclic butatrienes. The intermediate 1,2,3-cyclooctatriene was not directly detected by NMR spectroscopy.

1,2-Cyclopentadiene remains an elusive molecule. A logical precursor to this compound, 1-chloro-5-trimethylsilylcyclopentene, decomposes in the polar solvents typically employed in  $\beta$ -elimination reactions of halosilanes. Synthesis of a substituted 1,2-cyclopentadiene, 1-phenyl-1,2-cyclopentadiene, has also proven unsuccessful. The precursor to this strained allene rearranges at -78°C.

The existence of 1,2-cyclobutadiene was examined using *ab*

*initio* calculations. This intermediate was viewed as forming through the degenerate rearrangement of vinylacetylene. Results of this study suggest that 1,2-cyclobutadiene is best represented as a planar diradical, rather than as a chiral allene.

## **GENERAL INTRODUCTION**

**This dissertation is divided into three separate chapters:**

**1) photocycloaddition of alkenes to arenes, 2) photochemical generation of carbenes, and 3) synthesis of strained cyclic cumulenes. Because the topics covered are so diverse, each chapter contains its own introduction, results and discussion, and conclusion. Therefore, a general introduction has been omitted.**

## **CHAPTER 1**

### **PHOTOCYCLOADDITION OF ALKENES TO ARENES**

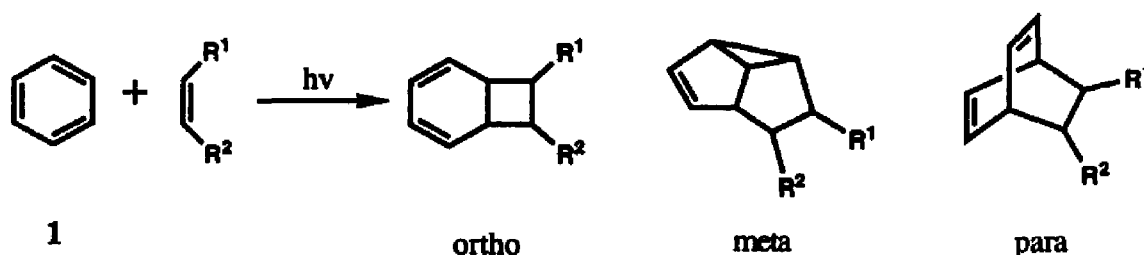
#### **INTRODUCTION**

Aromatic compounds were considered to be photochemically unreactive until 1957, when Bryce-Smith and Blair reported the formation of fulvene upon irradiation of benzene.<sup>1</sup> Subsequent investigations have revealed other photochemically-induced rearrangements of benzene, leading to isomerization products such as benzvalene<sup>2</sup> and prismane.<sup>3</sup> Work in this area encouraged explorations into other aspects of arene photochemistry, including addition and cycloaddition pathways.

The photochemical cycloaddition of an alkene to benzene was first reported by Angus and Bryce-Smith in 1959.<sup>4</sup> Since this initial discovery, numerous other examples of related photocycloadditions, involving olefins and aromatic substrates, have been identified. Two recent reviews detail many of these reactions, as well as discussing mechanistic possibilities for these cycloadditions.<sup>5</sup>

Photochemical reactions between benzene and olefins lead to the formation of three possible cycloadducts, which result from 1,2-(ortho), 1,3-(meta), and 1,4-(para) additions (Scheme 1). Ortho and meta products are predominant with benzene; ortho

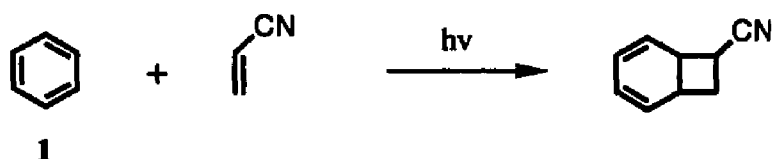
**Scheme 1**



products are favored when significant donor-acceptor interactions are possible. A general guideline, delineated by Bryce-Smith, predicts the formation of ortho adducts when the difference in ionization potential ( $\Delta$  I.P.) between the alkene and arene is greater than 0.6 eV.<sup>6</sup> While this is a useful generalization, exceptions have been noted.<sup>7</sup> The reaction of benzene (donor) with acrylonitrile (acceptor) gives predominantly 1,2-addition products (Scheme 2).<sup>8</sup> The difference in ionization potential in this case is 1.04 eV. The

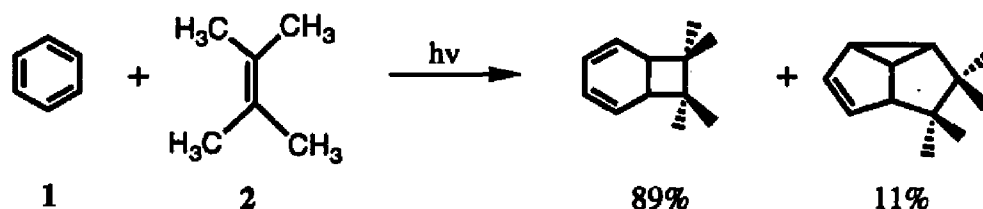


## Scheme 2



converse situation is also favorable, as in the case of benzene (acceptor) and tetramethylethylene (donor), where  $\Delta I.P. = 0.94$  (Scheme 3).<sup>6</sup>

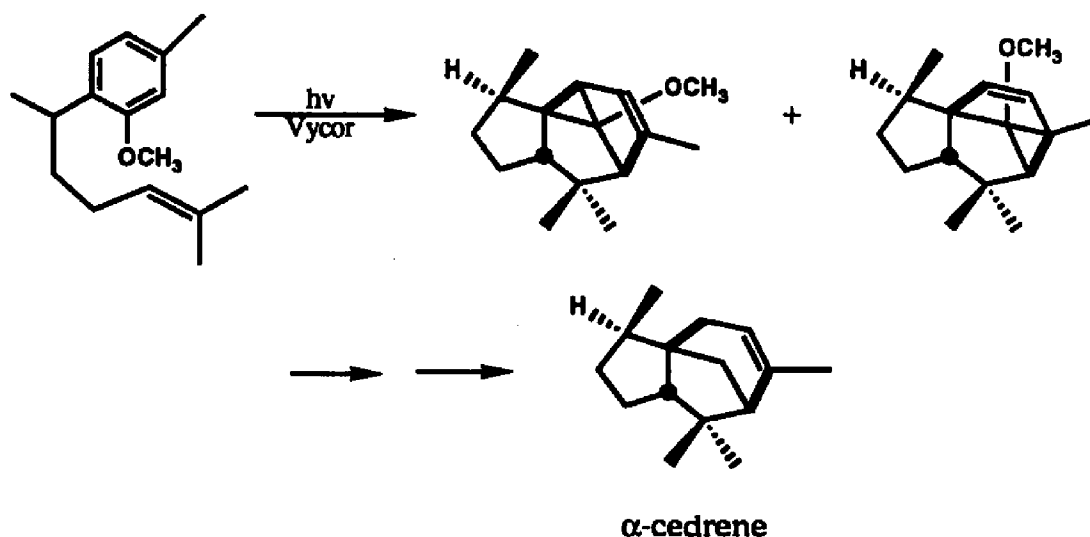
## Scheme 3



The meta cycloaddition of alkenes to benzene can result in products which are quite complex; formation of three new rings and the introduction of up to six contiguous stereocenters occurs in a single step. This approach has proven useful in the synthesis of natural products, as demonstrated by Wender in the synthesis of  $\alpha$ -cedrene (Scheme 4).<sup>9</sup>

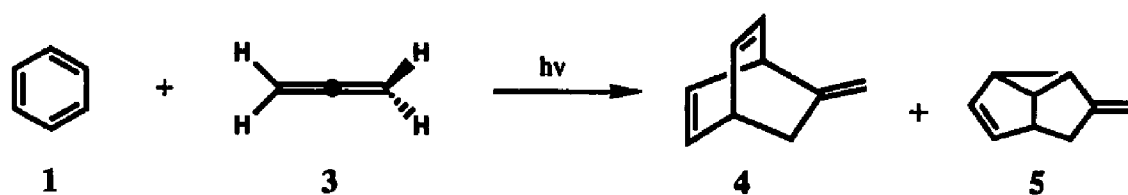
Few 1,4-additions of alkenes to benzene have been reported in the literature. The only olefinic derivatives which favor para addition are the allenes. The addition of allene to benzene, for

#### Scheme 4



example, gives meta and para addition products in a 1:2 ratio, respectively (Scheme 5).<sup>10</sup> Similarly, irradiation of benzene and 1,2-cyclononadiene resulted in a 6:1 product ratio of para to meta cycloadducts.<sup>11</sup>

#### Scheme 5



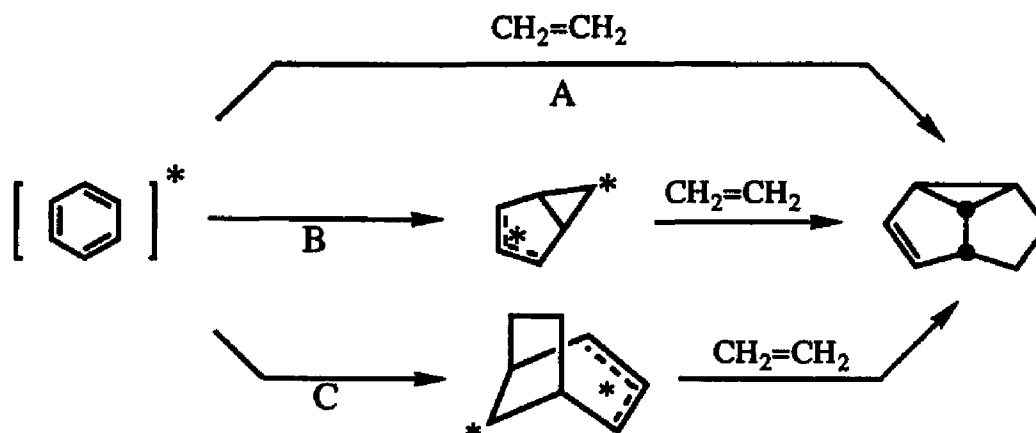
Mechanistically, these cycloadditions are believed to occur from the lowest excited singlet state of benzene. Ortho and para additions from this  $^1B_{2u}$  state are orbital-symmetry forbidden,

unless charge transfer is involved. The I.P. trends noted for ortho addition products lend credence to the involvement of a charge-transfer intermediate.

Meta cycloadditions have been described as following three potential mechanistic pathways (Scheme 6).<sup>5b</sup> Path A, a fully concerted mechanism, is considered unlikely, due to the considerable bond reorganization which would be required, and the inability of this mechanism to explain the high observed regioselectivity in these reactions. Rearrangement of benzene to a "prefulvene" diradical prior to alkene addition (Path B) has been discounted through both labelling<sup>12</sup> and computational<sup>13</sup> studies, but certainly cannot be ruled out. Mechanism C, requiring initial formation of an exciplex prior to bond closure, has received support from labelling experiments,<sup>12</sup> quenching studies,<sup>14</sup> and theoretical approaches.<sup>13, 15</sup>

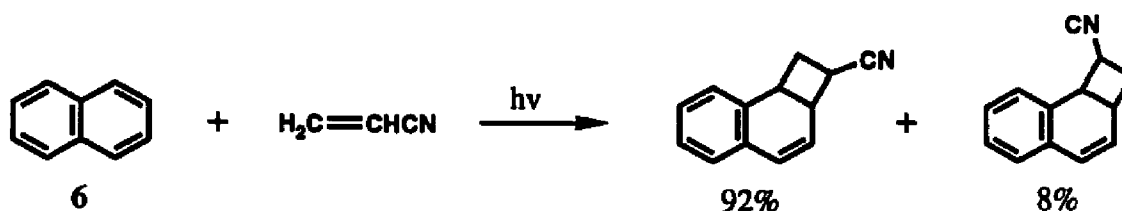
Para cycloadducts are quite rare in benzene-alkene photoreactions. Computational chemistry suggests that poor spatial overlap between the arene and alkene  $\pi$  bonds may account for the paucity of these products.<sup>15</sup>

**Scheme 6**



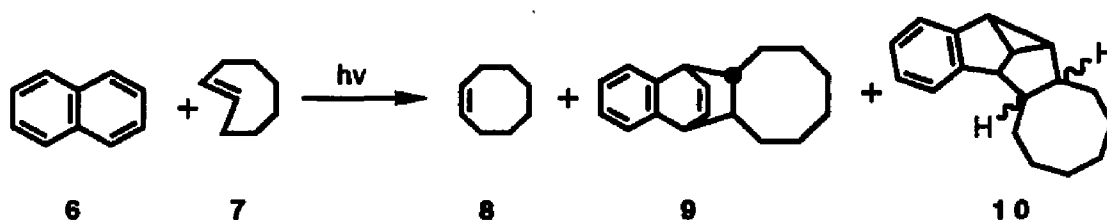
Naphthalene and its derivatives, in contrast with benzene, favor ortho and para addition products upon photolysis in the presence of olefins; meta cycloaddition products are rather unusual. The most commonly observed products contain cyclobutane rings, resulting from 1,2-addition of alkenes to naphthalenes. A nitrile substituent, either on the olefinic or naphthalenic moiety, has been found to enhance reactivity (Scheme 7).<sup>16</sup>

**Scheme 7**



Inoue *et al.* have reported both para and meta addition products, albeit in low yield, upon irradiation of naphthalene with trans-cyclooctene. The primary process occurring during this reaction is the photoisomerization of trans-cyclooctene to cis-cyclooctene (**Scheme 8**).<sup>17</sup> Under the same reaction conditions, cis-cyclooctene yielded no addition products during irradiation with naphthalene. Quenching studies indicated the trans alkene quenched the naphthalene singlet thirty times faster than its cis counterpart.

**Scheme 8**



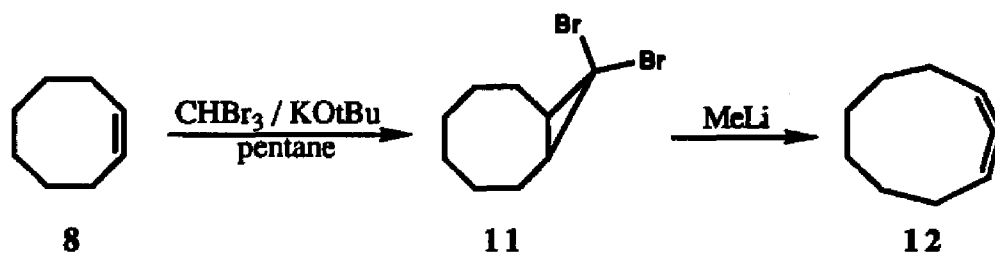
The addition of olefins to naphthalene has been proposed to occur via the naphthalene singlet excited state. Fluorescence quenching studies have suggested that a polar exciplex is involved in the reaction of naphthalene and acrylonitrile; however, an ion-pair mechanism may be operative in the reaction of 1-naphthonitrile with tetramethylethylene.<sup>18</sup> Product distribution for naphthalene-

alkene additions are dependent upon solvent polarity, irradiating wavelength, and percent conversion.

## Results and Discussion

Our interest in arene-olefin photocycloaddition initially revolved around the addition of 1,2-cyclononadiene to naphthalene. The addition of allenes to benzene has been documented, but the reaction of allenes with naphthalene has never been explored. The allene selected for this study was 1,2-cyclononadiene, chosen because of its stability and ease of synthesis. 1,2-Cyclononadiene is the smallest, unsubstituted cyclic allene which is stable at room temperature; it was synthesized by the Skattebol procedure (Scheme 9).<sup>19</sup>

**Scheme 9**

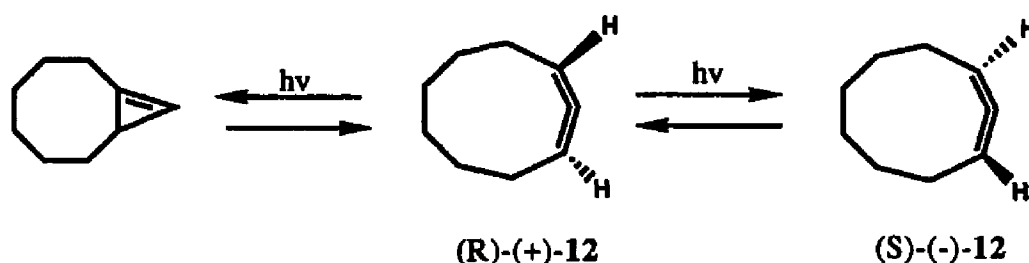


Allenes undergo their own collection of singlet photoreactions.

The two chief processes observed for these cumulenes are  $\pi$ -bond

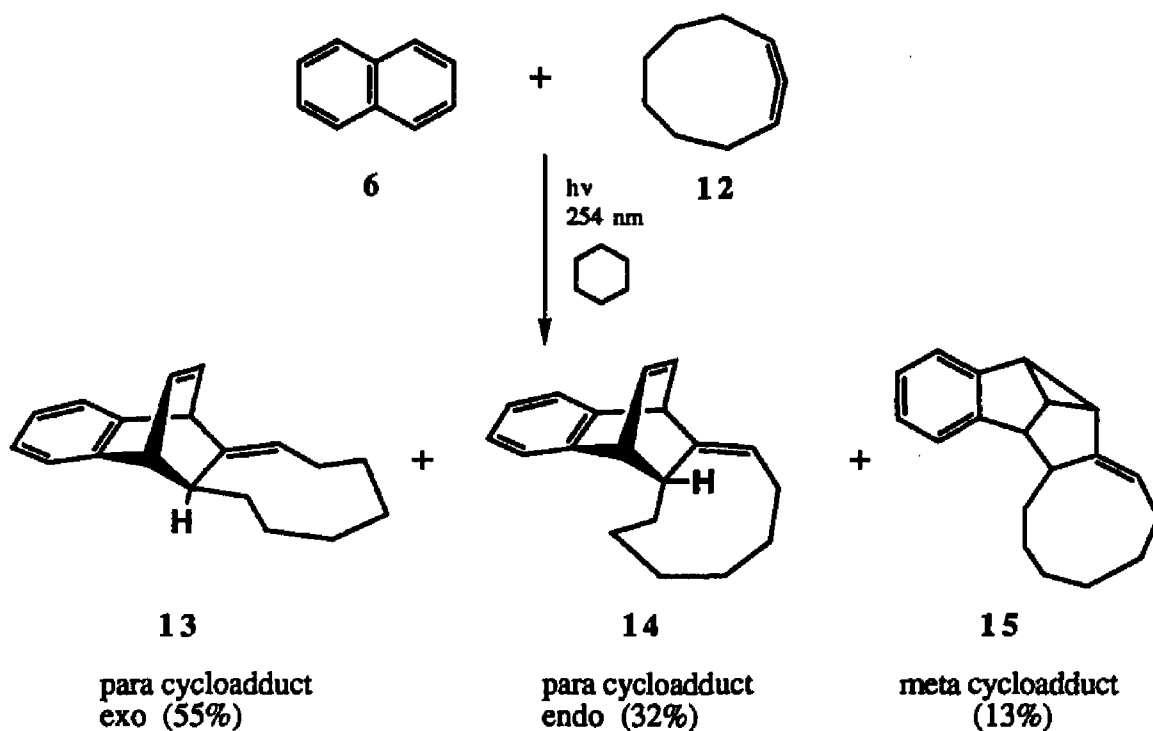
rotation and 1,2-hydrogen migration. Photolysis of optically active 1,2-cyclononadiene, for example, yields both the racemized and rearranged products (**Scheme 10**).<sup>20</sup> In the present case, allene photoreactions are not expected, since light is absorbed by the naphthalene.

**Scheme 10**



A cyclohexane solution of naphthalene and 1,2-cyclononadiene was irradiated in a Rayonet apparatus at 254 nm. The progress of the reaction was monitored by TLC and NMR. Reaction was carried to low conversion in order to avoid secondary photochemistry. Three products were isolated by preparative gas chromatography and assigned the structures shown in **Scheme 11**. Structural assignment was based upon high-field NMR analysis, and by comparison with spectra of similar compounds. The two major isomers are the result of para cycloaddition, while the minor product arises from the rarely observed meta cycloaddition of the

# Scheme 11



diene to naphthalene. A high-field resonance ( $\delta$  0.27) integrating to one proton was used to distinguish the exo and endo products. This resonance implies an aliphatic proton tucked under either the aromatic ring or a double bond, a situation which occurs only with the endo cycloadduct. Olefinic protons for the endo adduct are found at  $\delta$  5.37 (9-membered ring) and  $\delta$  6.45 and 6.65 (bridge). The bridgehead hydrogens are located at  $\delta$  3.79 and  $\delta$  4.27. For the exo adduct, the olefinic protons appear as two overlapping



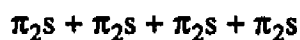
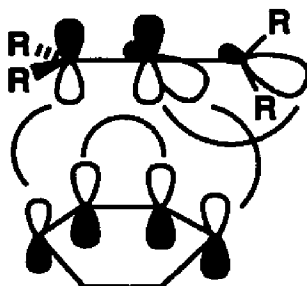
ddd at  $\delta$  6.55 (bridge), as well as another ddd at  $\delta$  5.35 (9-membered ring). The bridgehead hydrogens for this product occur at  $\delta$  3.86 and  $\delta$  4.28. These values compare favorably with those reported by Inoue for the addition of cyclooctene to naphthalene.<sup>17</sup>

Identification of the meta adduct was also made by comparison of its  $^1\text{H}$  NMR spectrum with that of known meta adducts. Significant resonances for compound 15 included a quartet at  $\delta$  2.96 and a doublet at  $\delta$  3.28. Meta adduct 10, reported by Inoue, displayed a quartet at  $\delta$  2.85 and a doublet at  $\delta$  3.15.<sup>17</sup> A pure sample of adduct 15 has not been obtained, however, because of overlap with the endo product during prep GC.

In orbital symmetry terms, the formation of para adducts is a forbidden six-electron ( $\pi 2_s + \pi 4_s$ ) process. The reaction is allowed, however, when viewed as an eight-electron process, which would require participation of the second allenic double bond in the reaction (Figure 1). This rationalization has basis in allene thermal chemistry; the commonly observed [2 + 2] thermal addition of ethylene to allene can be considered an allowed six-electron

process through participation of the second allenic bond.<sup>20</sup>

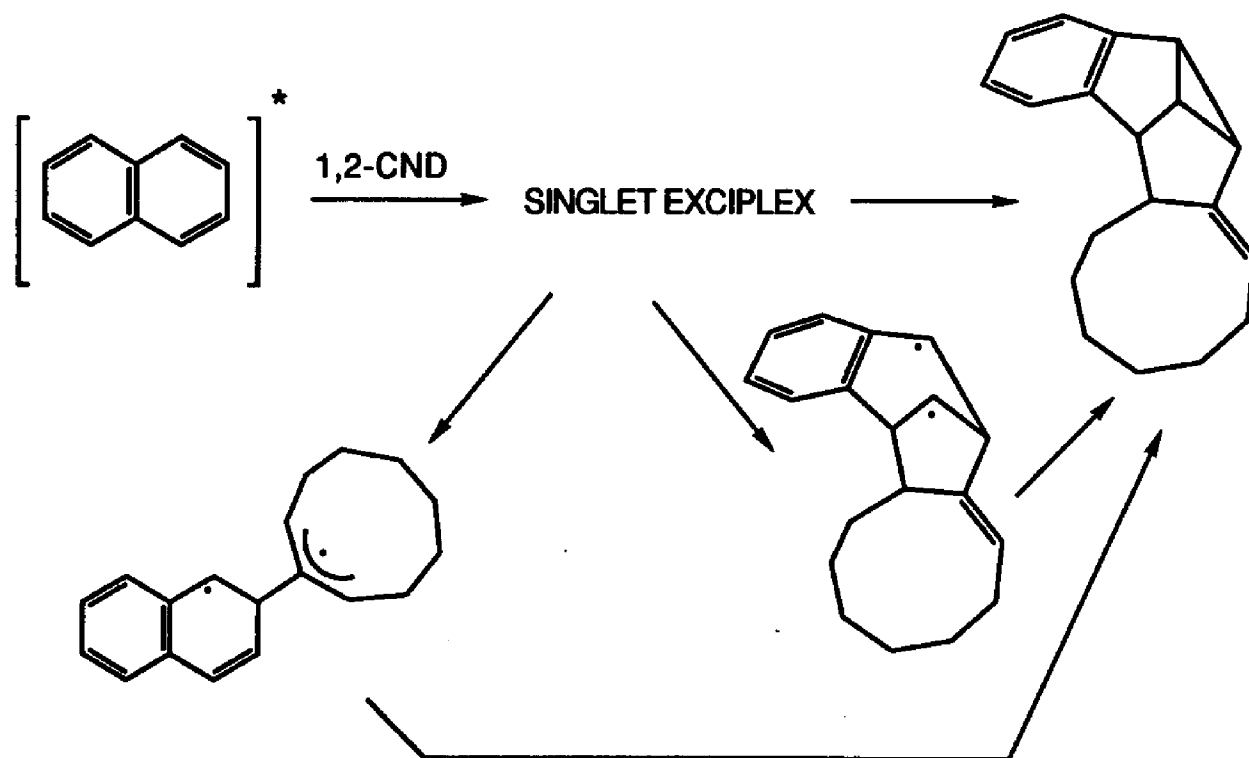
**Figure 1**



By analogy with benzene cycloadditions, the meta adduct is proposed to form via a singlet exciplex. Two biradical intermediates can be envisioned, both of which close to give the observed product (**Scheme 12**).

In order to further explore the scope of allene-arene photoadditions, several related reactions were examined. When naphthalene and 1,2-nonadiene were irradiated under conditions identical to those employed in the case of 1,2-cyclononadiene, no detectable photoadducts were observed (**Scheme 13**). The reason for this difference in reactivity was not readily apparent, although 1,2-nonadiene may not quench the naphthalene excited state as efficiently as 1,2-cyclononadiene.

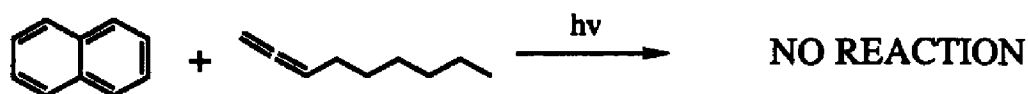
Anthracene was also irradiated along with 1,2-cyclononadiene



Scheme 12

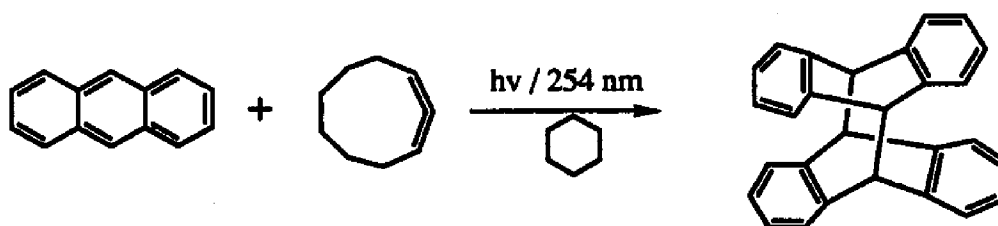
in a benzene solution. A highly-insoluble, white solid was obtained

**Scheme 13**



following 21.5 hours irradiation, presumably the anthracene dimer (Scheme 14). No photoadducts resulting from anthracene-alkene cycloaddition were detected.

**Scheme 14**



**Conclusion**

In general, the addition of olefins to naphthalene favors formation of ortho products. The photoaddition of 1,2-cyclononadiene to naphthalene, however, gave para adducts as the major products, along with a small amount of the meta cycloadduct. The reaction can be considered to be an orbital symmetry allowed eight-electron process, through participation of

both allenic bonds. The lack of reactivity on the part of 1,2-nonadiene was unexpected. Quenching studies may demonstrate that the acyclic allene is a poor quencher when compared with 1,2-cyclononadiene, although other factors may contribute to the quenching of singlet naphthalene. The photoaddition of 1,2-cyclononadiene to anthracene was hindered by the tendency of the aromatic substrate to dimerize. In summary, this project affords a rare example of 1,4-addition of an allene to naphthalene.

## CHAPTER 2

### PHOTOCHEMICAL GENERATION OF CARBENES

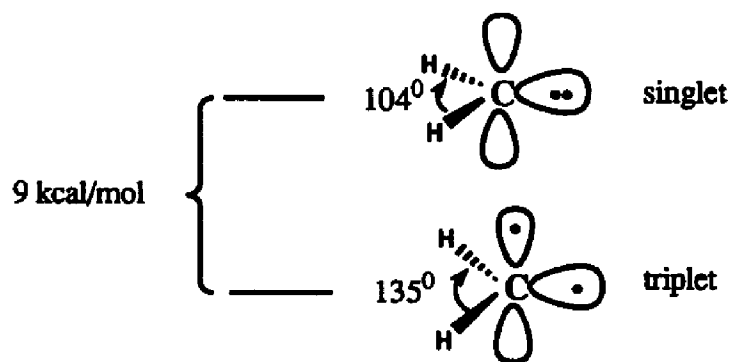
#### INTRODUCTION

Carbenes are neutral, divalent, reactive intermediates, which have been studied by chemists for over eighty years.<sup>22</sup> Due to the fleeting existence of these species, investigations into structure/reactivity relationships have proven challenging. Increased understanding of the chemistry of carbene intermediates has evolved through the use of sophisticated experimental techniques, as well as advanced computational models.

The simplest carbene known is methylene,  $\text{:CH}_2$ . The ground state structure of methylene was debated until 1976, when Lineberger and coworkers employed laser photoelectron spectroscopy to unambiguously determine that the triplet is approximately 9 kcal/mol lower in energy than the singlet (Figure 2).<sup>23</sup> Computational studies on methylene have confirmed that the triplet is indeed the ground state.<sup>24</sup> Note that

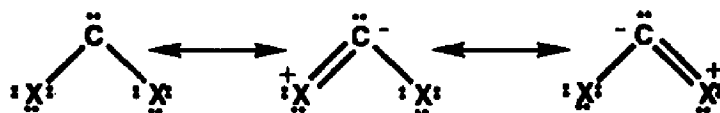
both structures are bent, a deviation from the previous notion that the triplet possessed a linear geometry.

**Figure 2**



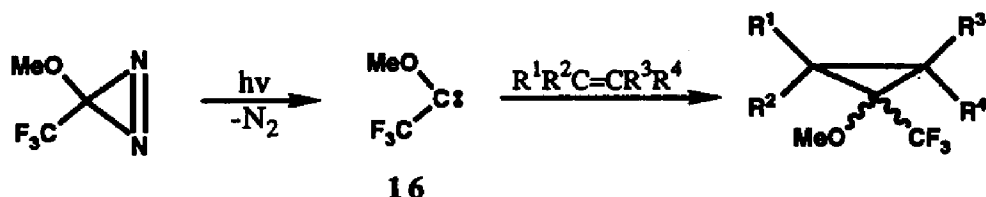
Substituents on methylene affect the order of singlet and triplet states. Singlet ground states are favored by electron-donating groups, such as a methoxy substituent, as well as by the halogens. The stabilization of the singlet relative to the triplet can be ascribed to two factors: resonance stabilization, in which electrons are donated into the empty p orbital (Figure 3), and inductive electron withdrawal through  $\sigma$ -bonds. Moss and

**Figure 3**



coworkers recently tried to increase carbenic stability and selectivity by incorporating both an electron donating group (methoxy) and an inductively withdrawing substituent (trifluoromethyl) into the carbene.<sup>25</sup> This "push-pull" carbene stabilization was, however, unsuccessful; methoxytrifluoromethylcarbene (**16**) proved to be highly reactive and quite indiscriminate in additions to alkenes (Scheme 15).

**Scheme 15**

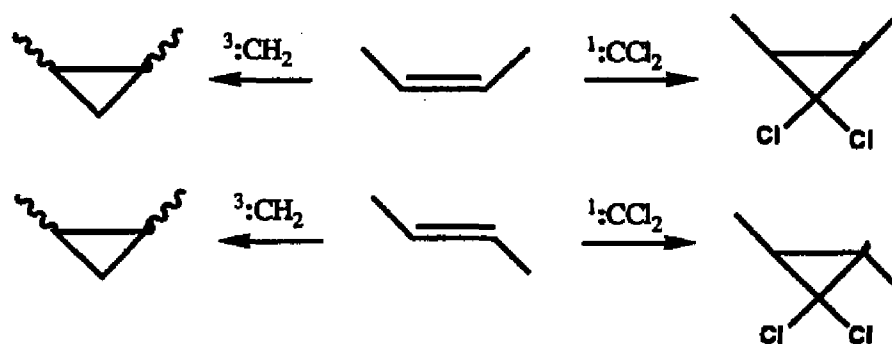


In general, carbenes follow the reactivity/selectivity principle. The more reactive the carbene, the less selective, and vice versa. Methylene,  $\text{:CH}_2$ , is so reactive that, in 1956, Doering described methylene as "the most indiscriminate reagent known in organic chemistry."<sup>26</sup> Substituted carbenes are more selective than methylene and, consequently, react more slowly. The electronic ground state of a carbene strongly affects its reactions. In the addition of carbenes to alkenes, Skell postulated that singlet carbenes add stereospecifically, while triplet carbenes add



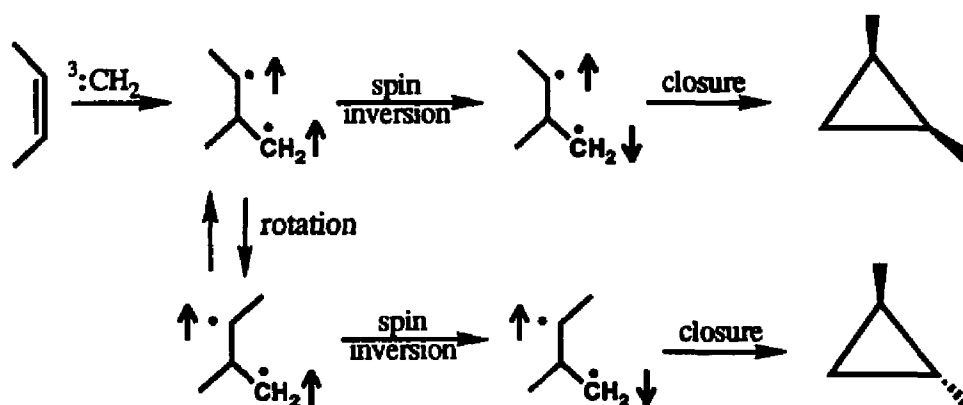
nonstereospecifically.<sup>27</sup> Dichlorocarbene, a singlet, adds stereospecifically to cis- and trans-2-butene, while methylene, a triplet, adds in a nonstereospecific fashion (Scheme 16).<sup>28</sup>

**Scheme 16**



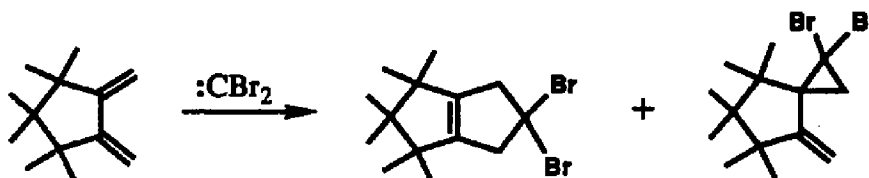
Triplet carbenes can, however, add to olefins stereospecifically; since the addition is a two-step process, a single product will be obtained if closure of the intermediate diradical is faster than bond rotation (Scheme 17).

**Scheme 17**



In a few instances,<sup>29</sup> carbenes have added to 1,3-dienes to give products which result from 1,4-addition of the carbene to the conjugated system (**Scheme 18**).<sup>30</sup> The normal 1,2-cycloaddition adducts are also obtained from these

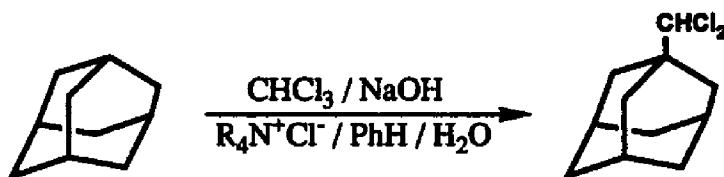
**Scheme 18**



reactions. Although it is an orbital-symmetry allowed process, 1,4-addition appears quite rare. Recent evidence suggests that this addition involves the free carbene, which adds to the diene in a concerted fashion.<sup>29</sup>

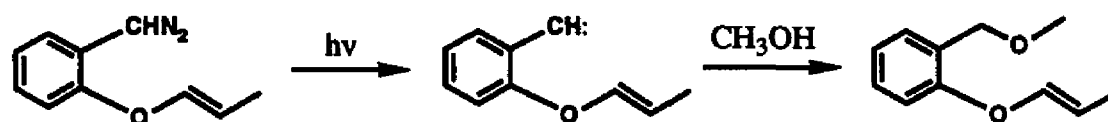
Another important reaction of carbenes is bond insertion, most notably into carbon-hydrogen bonds. Singlet carbenes are proposed to insert directly into C-H bonds, as illustrated in **Scheme 19** for the insertion of dichlorocarbene into

**Scheme 19**



adamantane.<sup>31</sup> A frequently employed trap for singlet carbenes is methanol; this yields products which result from carbene insertion into an O-H bond (**Scheme 20**).<sup>32</sup>

**Scheme 20**



Triplet carbenes also insert into C-H bonds. The putative mechanism involves initial hydrogen abstraction, followed by recombination of the newly formed diradical pair. Evidence for this mechanism has been offered by Closs and Closs through CIDNP experiments on diphenylcarbene (**Scheme 21**).<sup>33</sup>

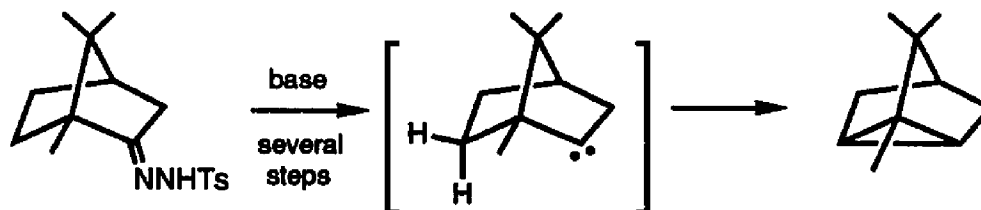
**Scheme 21**



Numerous rearrangements which involve carbenes have been identified. Perhaps the most common rearrangement is a 1,2-hydrogen shift, which can be viewed as an intramolecular C-H insertion. The key step in the Bamford-Stevens reaction depicted in **Scheme 22** involves an intramolecular C-H insertion, in the form of

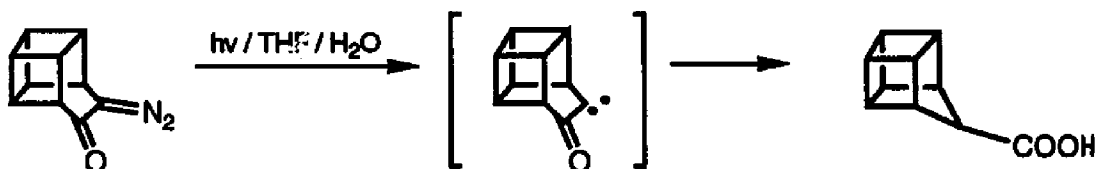
a 1,3-hydrogen shift.<sup>34</sup> Alkyl and aryl groups also migrate, though not as readily as hydrogen.

**Scheme 22**



The Wolff rearrangement is another synthetically useful carbene-based rearrangement. This rearrangement occurs upon photolysis or thermolysis of  $\alpha$ -diazo-carbonyl compounds and produces ketenes, which are ultimately converted to acids or esters (Scheme 23).<sup>35</sup>

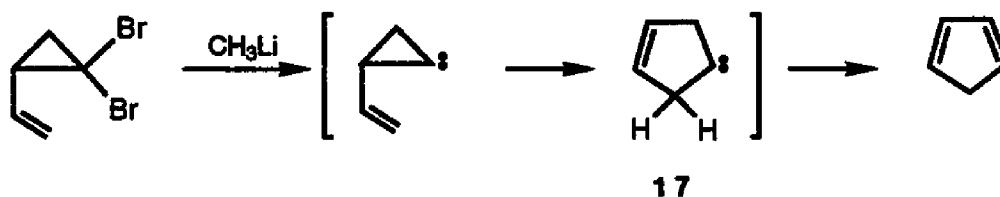
**Scheme 23**



The Skattebol rearrangement occurs commonly in vinylcyclopropylidenes. Two rearrangements are operative during this reaction: the first leads to formation of

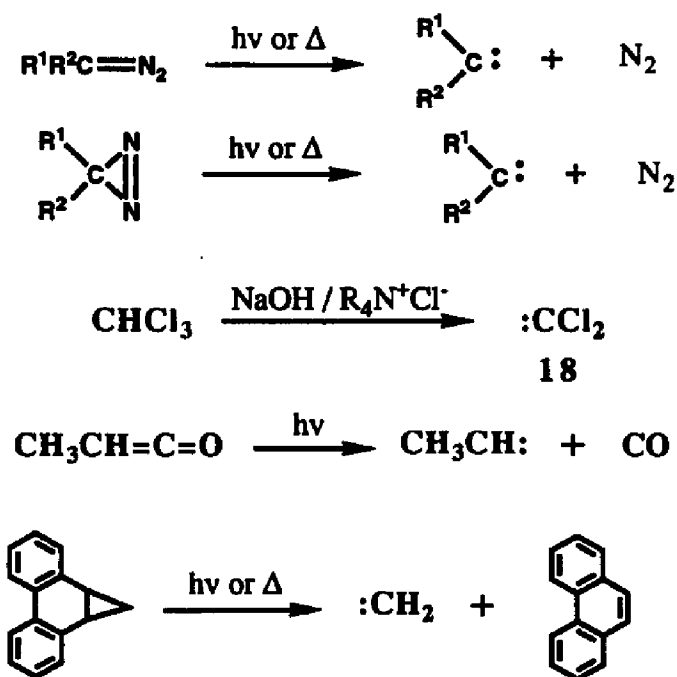
cyclopentenylidene **17**, and the second, a 1,2-H migration, gives the cyclopentadiene product (Scheme 24).<sup>36</sup>

**Scheme 24**



Although numerous methods have been developed for carbene generation (Scheme 25), the two most commonly utilized are photolytic or thermolytic decomposition of diazirines and diazo compounds. In particular, the decomposition of diazirines displays remarkable versatility in generating carbenes. This is due to the wide variety of substituents which can be incorporated into the carbene precursor.<sup>37</sup> Dichlorocarbene (**18**) is generally prepared by combining chloroform with a strong base under phase-transfer conditions.<sup>38</sup> Other, less frequently used, methods for generating carbenes include decomposition of ketenes<sup>39</sup> and carbene extrusion from small rings.<sup>40</sup>

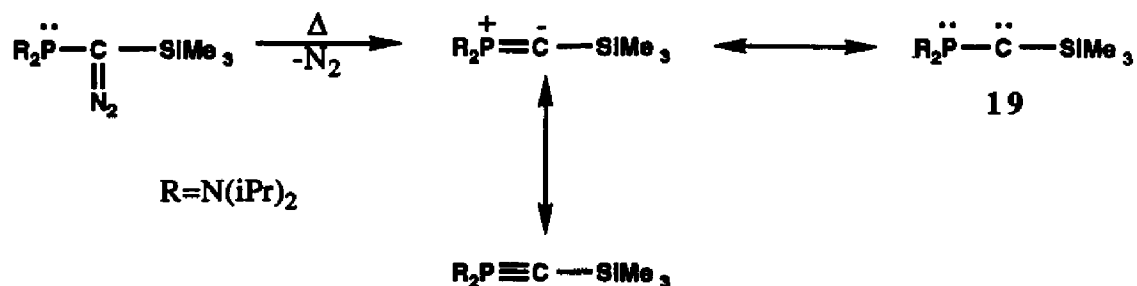
## Scheme 25



Although carbenes are generally considered to be reactive intermediates, two recent reports in the literature have purported the synthesis of stable carbenes.<sup>41</sup> Bertrand and coworkers reported the isolation of a distillable phosphinocarbene (19), which is stabilized by the lone pair of electrons on phosphorous (Scheme 26).<sup>42</sup>

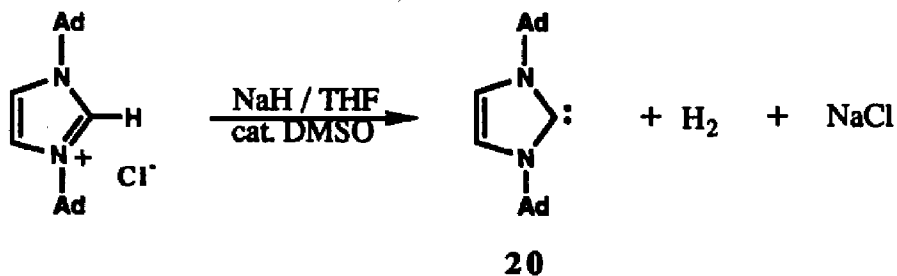
A stable, crystalline carbene has reportedly been synthesized by Arduengo *et al.* (Scheme 27).<sup>43</sup> The buttressing effect of the adamantyl groups is largely responsible for the isolability of

### Scheme 26



compound **20**. Electronic stabilization is imparted by resonance interactions with the adjacent nitrogen lone pairs. X-ray crystallography supports the divalent carbene structure of this compound; however, experiments to determine if this crystalline compound *reacts* like a carbene have yet to be reported.

### Scheme 27



## **RESULTS AND DISCUSSION**

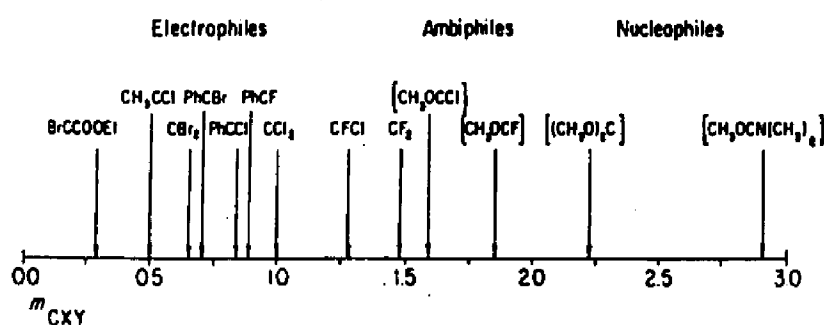
### **DICHLOROCARBENE**

The peculiar electronic structure of singlet carbenes results in a "split personality" of reactivity. Because carbenes possess a sextet of electrons, rather than an octet, they are expected to exhibit electrophilic behavior. On the other hand, carbenes also contain a "lone pair" of nonbonding electrons, implying that they can also behave as nucleophiles. In 1980, Moss developed a carbene selectivity index, which he described as "an empirical correlation of carbenic selectivity toward alkenes."<sup>44</sup> A standard set of alkenes was chosen for the cyclopropanation reactions, and dichlorocarbene was selected as the standard carbene with selectivity = 1.0. Carbenes whose selectivity is less than 1 are less selective, and more reactive, than dichlorocarbene; those carbenes whose selectivity is greater than 1 are more selective, therefore, less reactive, than :CCl<sub>2</sub>. Competition experiments were run between dichlorocarbene and numerous other singlet carbenes to determine which carbene was more selective in the cycloaddition reactions. The carbene selectivity spectrum which was compiled from these



experiments is reproduced in **Figure 4**. Electrophilic carbenes react most readily with electron-rich alkenes, while nucleophilic carbenes react fastest with electron-poor olefins. A carbene is defined as ambiphilic when it adds to both electron-rich and electron-poor alkenes.

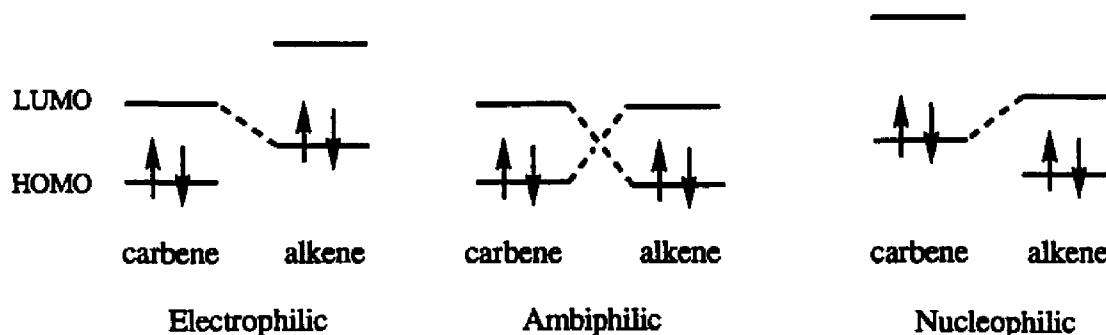
**Figure 4. Carbene Selectivity Index.**<sup>44</sup>



The "philicity" of carbenes can be explained through frontier molecular orbital (FMO) theory. In this scenario, carbene behavior is dictated by the dominant interactions:  $LUMO_{\text{carbene}} / HOMO_{\text{alkene}}$  or  $HOMO_{\text{carbene}} / LUMO_{\text{alkene}}$ . When the dominant interaction involves the  $LUMO_{\text{carbene}} / HOMO_{\text{alkene}}$ , the carbene behaves in an electrophilic manner. The reverse situation, in which  $HOMO_{\text{carbene}} / LUMO_{\text{alkene}}$  predominates, leads to nucleophilic addition of the carbene to the alkene. Finally, ambiphilic behavior is observed when the HOMO-LUMO energies for *both* the carbene and olefin are approximately the

same (Figure 5).<sup>44a</sup> In each case, the dominant interactions are shown by dotted lines.

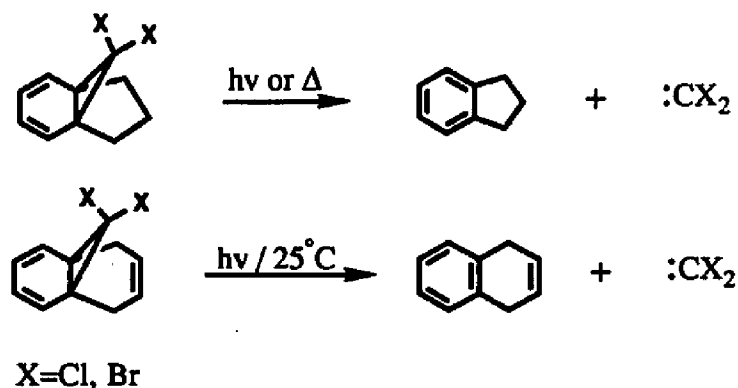
**Figure 5**



In spite of its central role as the "standard" carbene for the carbene selectivity index, the absolute rate constants for the addition of dichlorocarbene to a series of alkenes had never been measured. The inability to cleanly generate dichlorocarbene photochemically has been the chief stumbling block to kinetic studies in this area. Two photochemical dichlorocarbene precursors have been introduced during the past few years, although neither one had been applied to kinetic studies of dichlorocarbene (Scheme 28).<sup>45</sup>

In the present work, we developed an alternative photochemical precursor to dichlorocarbene. It is well known that

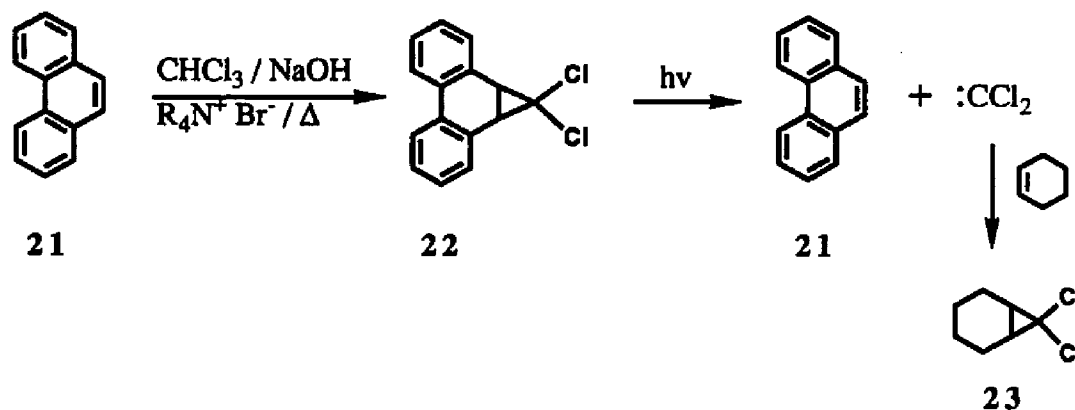
## Scheme 28



dichlorocarbene, generated under phase-transfer conditions, readily adds to phenanthrene.<sup>46</sup> What was not known, however, but has been established by our group, is that this adduct cleanly regenerates dichlorocarbene upon photolysis (**Scheme 29**). The formation of dichlorocarbene was established by trapping this intermediate with cyclohexene, thus producing the well-characterized compound dichloronorcaradiene. In effect, phenanthrene becomes a "carbene storage device."

Through a fortuitous encounter at a Gordon Conference, we became acquainted with John Chateauneuf at the University of Notre Dame. Chateauneuf was attempting to measure the absolute kinetics for the addition of dichlorocarbene to a series of olefins, but was frustrated by the lack of a good photochemical carbene precursor. This led to a collaboration between our two groups.

### Scheme 29



In addition to the synthesis of the carbene precursor, we also determined the quantum yield for the photolysis of **22**. The quantum yield, defined in **Equation 1** is a measure of the efficiency of a photoreaction. A totally efficient reaction would have  $\Phi=1$ . The

#### Equation 1

$$\Phi = \frac{\text{mmol product formed}}{\text{mE light absorbed}}$$

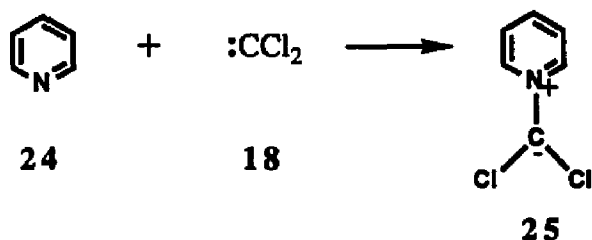
quantum efficiency, as determined on an optical bench with the use of ferrioxalate actinometry,<sup>47</sup> was 0.078 for a  $1 \times 10^{-3}$  M hexane solution irradiated at 280 nm. In determining the quantum yield, it was noted that the value of  $\Phi$  decreased with increasing irradiation time. This was expected, since more phenanthrene is produced during prolonged irradiation. Phenanthrene, being a stronger chromophore than adduct **22**, absorbs more light, thereby decreasing

the amount of light available for carbene generation.

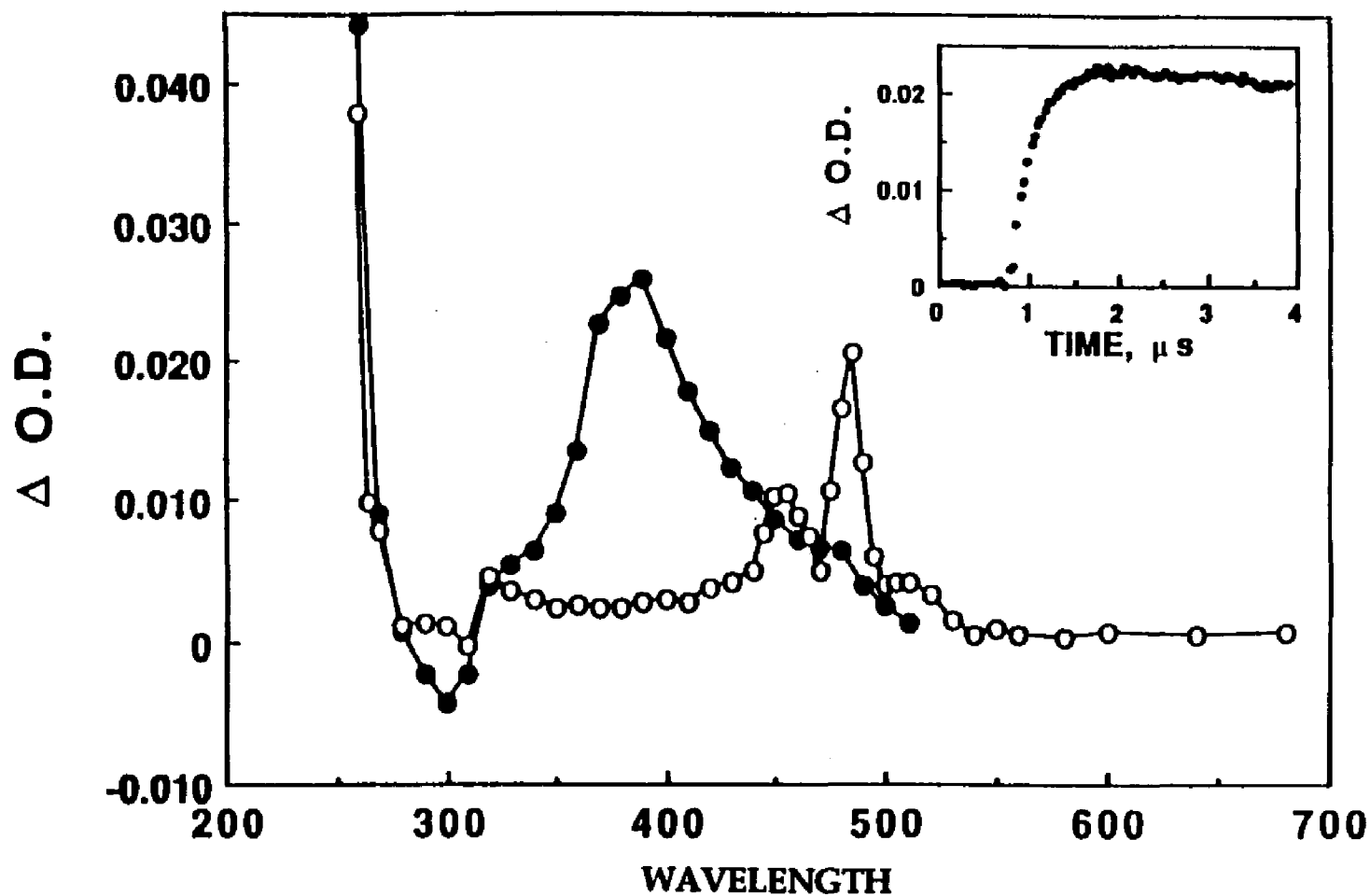
Chateauneuf utilized laser flash photolysis in an effort to directly detect dichlorocarbene in solution. Irradiation at 266 nm of a  $5 \times 10^{-5}$  M solution of **22** in cyclohexane produced UV absorption bands attributable solely to phenanthrene. No bands which could be assigned to  $\text{:CCl}_2$  were observed (**Figure 6**).

A technique for observing "invisible" singlet carbenes has been pioneered by Platz and coworkers.<sup>48</sup> This approach exploits the reaction of singlet carbenes with pyridine to form pyridinium ylides, species which absorb strongly in the UV (**Scheme 30**). The pyridinium ylide technique has been successfully employed in kinetic

**Scheme 30**



studies of other singlet carbenes, which are otherwise undetectable by UV.<sup>49</sup> Laser flash photolysis of **22** and pyridine produced the pyridinium ylide of dichlorocarbene, which had a lifetime of 35  $\mu\text{s}$  and  $\lambda_{\text{max}} = 390$  nm (**Figure 6**). Triplet absorption bands arising from



**Figure 6.** Transient absorption spectra observed 1.02 and 1.13  $\mu s$  after 266-nm LFP of  $5 \times 10^{-5}$  M **22** in  $N_2$ -saturated  $C_6H_{12}$  (o) and  $1 \times 10^{-4}$  M **22** in air-saturated  $C_6H_{12}$  containing  $5.24 \times 10^{-4}$  M pyridine (•), respectively. Insert shows a representative single-exponential growth ( $k_{exptl} = 4.1 \times 10^6 s^{-1}$ ) of pyridinium ylide **25** monitored at 400 nm.

phenanthrene were suppressed by running the reaction in air-saturated cyclohexane. The bimolecular rate constant for the reaction of dichlorocarbene with pyridine was determined by monitoring the pseudo-first-order growth rate of the ylide ( $k_{\text{exptl}}$ ) at different pyridine concentrations (Equation 2). The rate of decay of  $\text{:CCl}_2$  in the absence of pyridine,  $k_0$ , was estimated from the intercept of the pyridine quenching plot to be  $1 \times 10^5 \text{ s}^{-1}$ , which results in  $k_p = (7.90 + 0.23) \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ .

#### Equation 2

$$k_{\text{exptl}} = k_0 + k_p [\text{pyridine}]$$

In order to obtain the absolute bimolecular quenching rate constants of dichlorocarbene with a series of olefins, a competitive probe technique was utilized. At an optimum pyridine concentration,  $1.23 \times 10^{-4} \text{ M}$ , changes in  $k_{\text{exptl}}$  were followed with added quencher (Equation 3).

#### Equation 3

$$k_{\text{exptl}} = k_0 + k_p [\text{pyridine}] + k_q [\text{olefin}]$$

The results are presented in Table 1. It is apparent that the classification of dichlorocarbene as an electrophilic carbene is justified, since  $\text{:CCl}_2$  reacts most rapidly with electron-rich olefins, and more slowly with electron-poor alkenes. This work represents the first time that the absolute kinetics of dichlorocarbene have been measured.

**Table 1.** Absolute Rate Constants for the Reaction of Dichlorocarbene with Olefins.

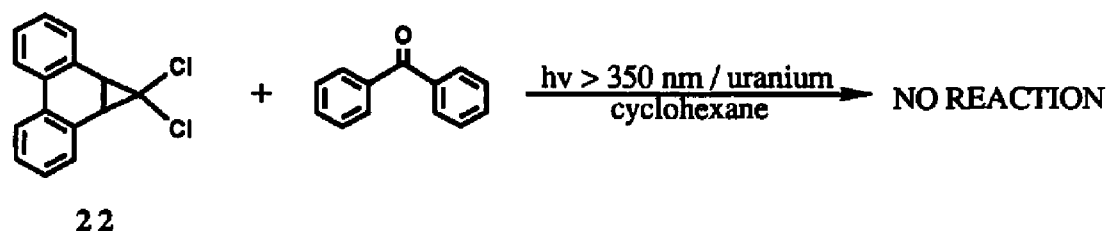
<u>Alkene</u>	<u>k, M<sup>-1</sup>s<sup>-1</sup></u>
$\text{Me}_2\text{C}=\text{CMe}_2$	$3.81 \times 10^9$
$\text{MeCH}=\text{CMe}_2$	$2.23 \times 10^9$
trans- $\text{MeCH}=\text{CHEt}$	$6.31 \times 10^7$
c- $\text{C}_6\text{H}_{10}$	$3.50 \times 10^7$
$\text{CH}_2=\text{CH-n-C}_4\text{H}_9$	$1.08 \times 10^7$

Having found a legitimate precursor for singlet dichlorocarbene, we thought it worthwhile to see if we could generate triplet dichlorocarbene through sensitization. The lowest



triplet state of dichlorocarbene is predicted to be 13.5 kcal/mol higher in energy than singlet  $\text{:CCl}_2$ .<sup>50</sup> The experiment was conducted by irradiating a cyclohexane solution of **22** and benzophenone at 350 nm through a uranium filter (**Scheme 31**). Since the dichloroadduct does not absorb light above 316 nm, and the uranium filter cuts off

**Scheme 31**



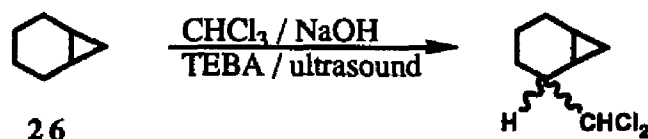
all light below 330 nm, benzophenone, with an absorption band at 340 nm, becomes the only chromophore absorbing light. Therefore, if any phenanthrene is produced in this reaction, it must come through triplet sensitization of **22**. After 12 hours irradiation, no phenanthrene had formed. Since energy transfer from benzophenone to **22** should be efficient, it appears that no triplet photodissociation of **22** occurs.

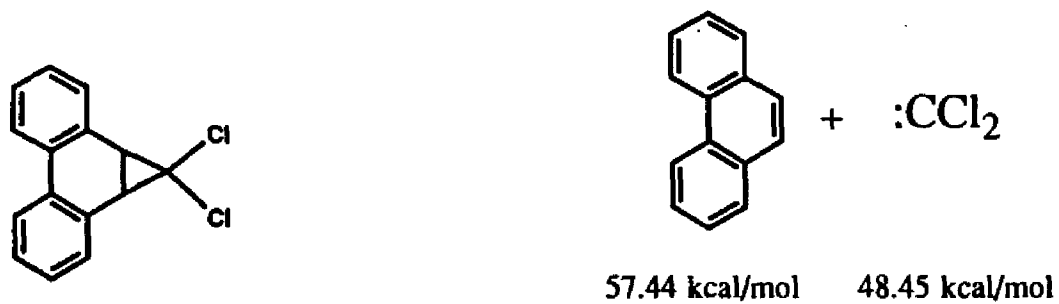
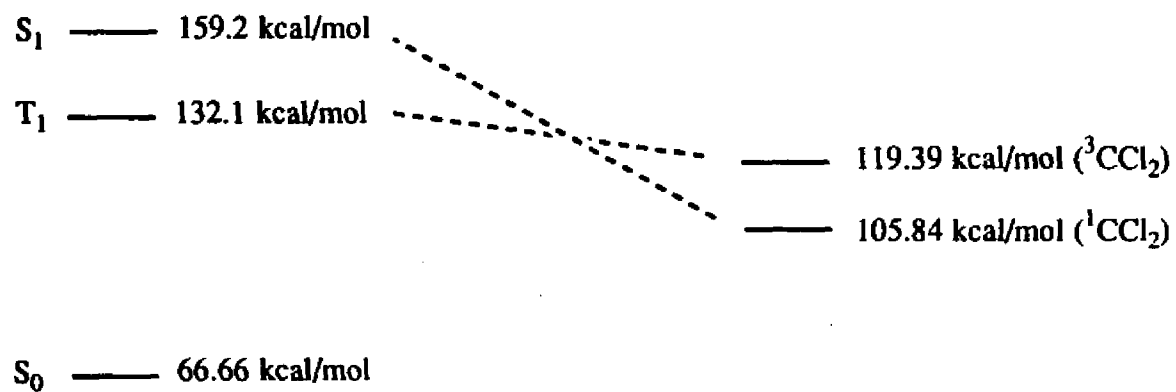
We examined the energetics of precursor **22**, phenanthrene, and dichlorocarbene in an effort to understand why no triplet sensitization was observed. The calculations were carried out on a SiliconGraphics work station using Spartan and the AM1 method.<sup>51</sup>

The triplet energy level for compound **22** was approximated by using the literature value for biphenyl. The energy level for the  $S_1$  state was calculated from the UV spectrum, while the singlet-triplet gap for dichlorocarbene was obtained from the literature.<sup>50</sup> The structures examined, along with their relative energies, are illustrated in **Figure 7**. Extrusion of singlet dichlorocarbene from the  $S_1$  state of adduct **22** is favored by 53.4 kcal/mol. For the triplet species, a 12.7 kcal/mol energy difference is predicted between adduct and carbene. Energetically, the singlet process is much more favorable than the triplet pathway. Similar results were obtained by applying Benson's additivity rules to these compounds.<sup>52</sup>

Dichlorocarbene is known to insert into C-H bonds, as in the previously cited reaction with adamantane.<sup>31</sup> In general, dihalocarbenes insert into tertiary and secondary C-H bonds of aliphatic compounds in low yields. In one recent example, Brinker and coworkers reported dichlorocarbene insertion exclusively into the secondary C-H site of **26** in 83% yield (**Scheme 32**).<sup>53</sup>

**Scheme 32**

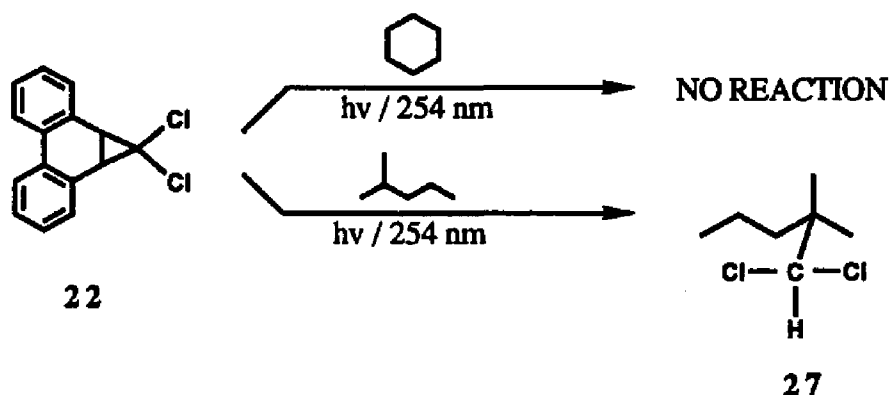




**Figure 7.** Energetics of dichlorocarbene extrusion from 22. All numbers are calculated (AM1) or estimated enthalpies of formation.

We chose to investigate the insertion of dichlorocarbene into C-H bonds. The hydrocarbons chosen for this study were 2-methylpentane and cyclohexane (**Scheme 33**). 2-Methylpentane was selected because it offers primary, secondary, and tertiary

**Scheme 33**

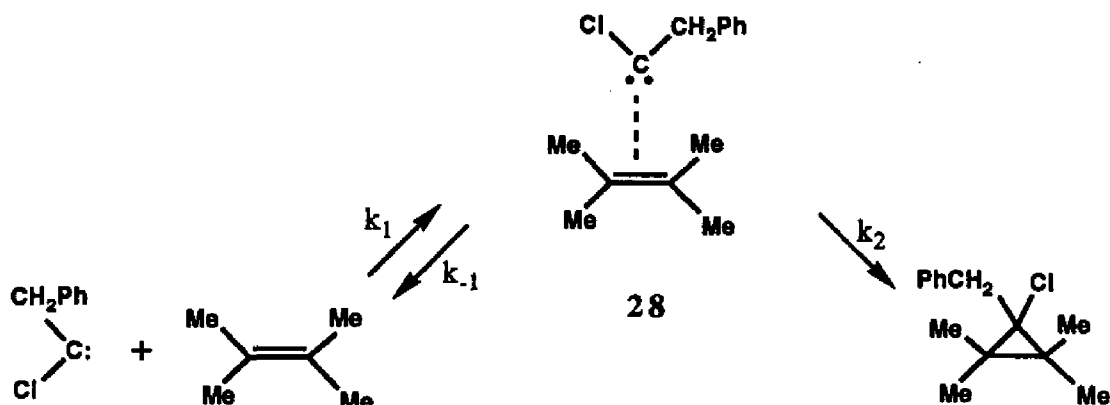


insertion sites. The irradiation was carried out through quartz at 254 nm, and monitored by TLC and HPLC. Photolysis of **22** and 2-methylpentane was conducted for 10 hours. Phenanthrene formation was noted during the course of the reaction. Upon NMR analysis, a singlet at  $\delta$  5.62 was attributed to the methine proton of **27**, which results from  $\text{:CCl}_2$  insertion into the tertiary C-H bond. Insertion of dichlorocarbene, generated by the Seyferth method, into 2-methylhexane, also gave a singlet at  $\delta$  5.62, again a result of insertion into the tertiary C-H bond.<sup>54</sup> No insertion of

dichlorocarbene into the less reactive methylene C-H bonds was observed upon irradiation of **22** with cyclohexane.

While some investigators believe carbene addition to alkenes occurs in a single step, others have proposed a multistep mechanism. Turro and Moss have proposed initial formation of carbene-alkene complex **28** (Scheme 34).<sup>55</sup> In the case of our carbene precursor, the presence of an alkene trap might be expected to increase the rate of phenanthrene formation. Such a suggestion is based upon initial dissociation of the precursor into a carbene-phenanthrene complex; in the presence of an alkene, recombination to form **22** would not be favored. In a merry-go-round experiment in the Rayonet, we irradiated **22** in the presence of cyclohexene, and, in separate quartz tubes, with added hexane. The amount of phenanthrene formed, determined from HPLC integration, was used as a measure of carbene generation. As can be seen in Table 2, phenanthrene was formed more rapidly in the hexane tubes, a finding which does not support development of a carbene complex. These experiments demonstrate that either a carbene-phenanthrene complex is not formed, or that the presence of a carbene trap does not affect said complex.

### Scheme 34

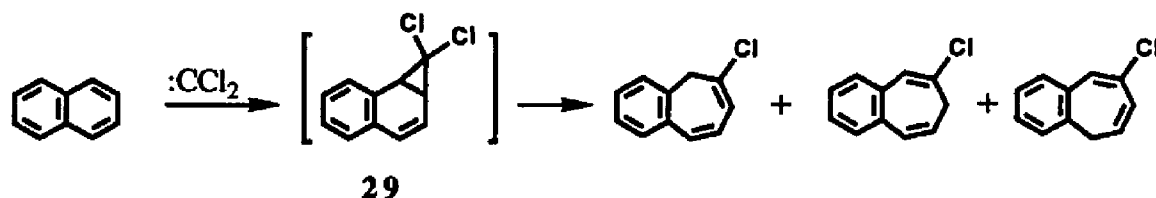


**Table 2.** Competition Study of Dichlorocarbene Between Hexane and Cyclohexene

<u>% Phenanthrene (Corrected)</u>			
<u>Solvent</u>	<u>2 min.</u>	<u>10 min.</u>	<u>20 min.</u>
hexane	1.10	3.52	4.85
hexane	1.02	3.38	4.52
cyclohexene	0.11	0.38	0.55
cyclohexene	0.10	0.39	0.57

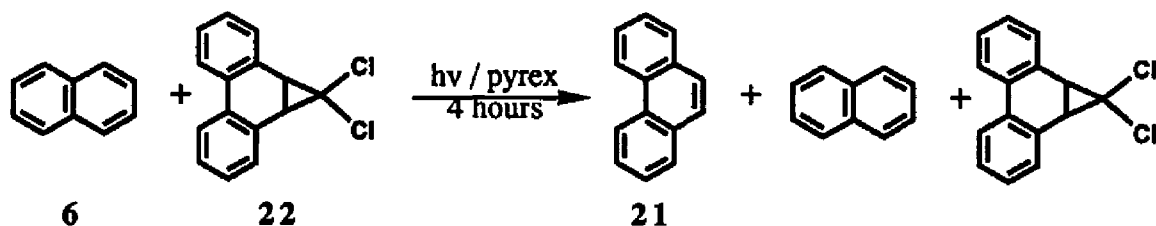
A number of isomers result upon addition of dichlorocarbene to naphthalene (Scheme 35).<sup>56</sup> The reaction presumably occurs through initial addition of the carbene to a double bond, followed by

**Scheme 35**



ring opening and loss of chloride ion. To date, the initial adduct **29** has not been observed. Our final investigation into the general utility of this new source of dichlororocarbene entailed the photochemical addition of  $\text{:CCl}_2$  to naphthalene. The present study was performed in an NMR tube, which was irradiated on the optical bench without the monochromator in order to maximize light intensity (**Scheme 36**). After four hours, the  $^1\text{H}$  NMR of this sample was remarkably clean, displaying peaks corresponding to **22**, naphthalene, and phenanthrene. No vinylic resonances, indicative of the cycloaddition product, were evident. We conclude that naphthalene may not be reactive enough to effectively trap dichlorocarbene.

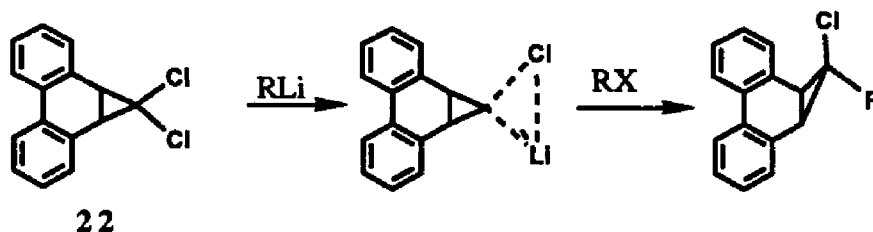
**Scheme 36**



## MONOCHLOROCARBENES

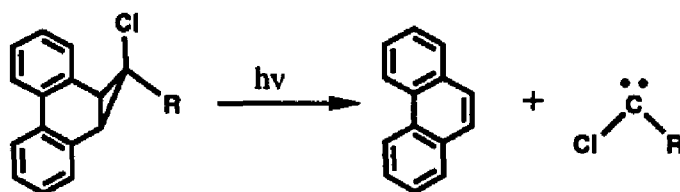
The quenching of carbenoids with alkyl halides is a well-documented reaction (**Scheme 37**).<sup>57</sup> We decided to explore the

**Scheme 37**



feasibility of utilizing readily synthesized **22** as a model compound in which one chloro substituent has been replaced by a proton or alkyl group. Photolysis of this new adduct would then form the corresponding carbene, while regenerating phenanthrene (**Scheme 38**).

### **Scheme 38**

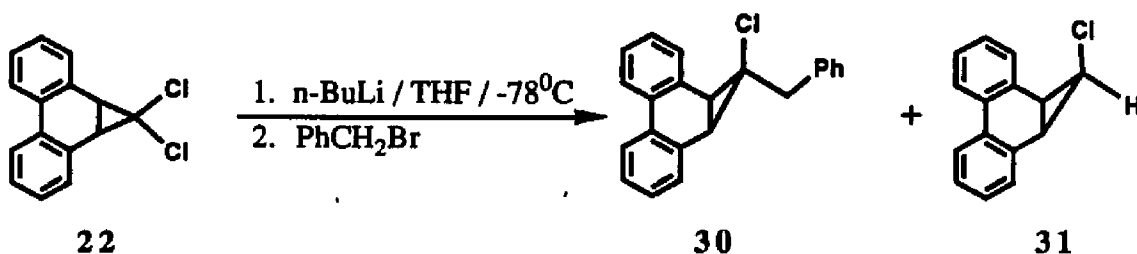


Our first target in this realm was benzylchlorocarbene, a well-characterized carbene which is readily accessible from its diazirine precursor.<sup>37</sup> Synthesis of this compound is depicted in **Scheme**



39. During the course of this and subsequent alkylation reactions, a

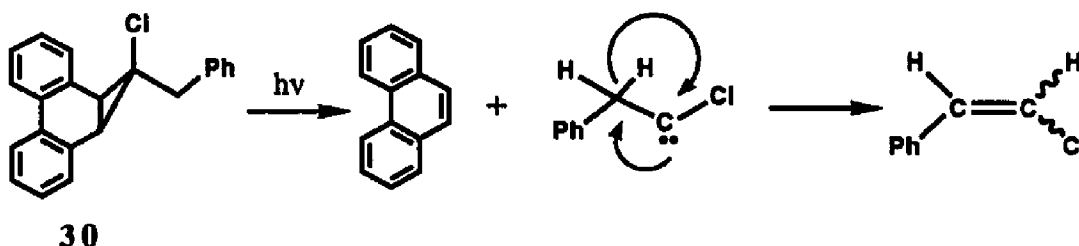
**Scheme 39**



spectacular teal color developed in the reaction mixture following addition of n-butyllithium. The source of this color is unknown; however, it was noted that if the tetrahydrofuran used was not distilled immediately prior to use, the green color did not develop. The desired benzylated product was obtained in 24% yield, along with a single monochloro product. The <sup>1</sup>H NMR spectrum for 30 was quite simple, displaying aromatic resonances, a singlet at  $\delta$  2.93 (benzylic protons), and a singlet at  $\delta$  3.39 (bridgehead protons). The monochloro adduct was assigned the endo chloro structure, based on a coupling constant of 7.7 Hz. Similar alkylation reactions favor products in which the alkyl moiety also occupies the exo position, primarily due to steric interactions. Separation of these two products was achieved by column chromatography on florisil, as these adducts were found to readily decompose on silica gel.

The photochemistry of **30** has been briefly explored. If **30** is a carbene precursor of benzylchlorocarbene, one would expect to observe phenanthrene formation upon photolysis, as well as the development of two known  $\beta$ -chlorostyrene isomers. These alkenes arise from a 1,2-H shift which occurs upon formation of the incipient carbene (Scheme 40).<sup>58</sup> The <sup>1</sup>H NMR spectrum of these

**Scheme 40**

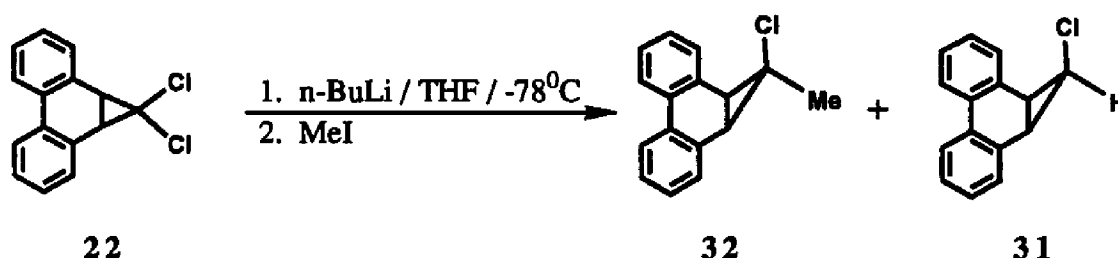


olefins would display four doublets in the vinylic region. Irradiation of a hexane solution of **30** at 254 nm gave rise to a mixture which displayed several olefinic resonances. Two distinct doublets, at  $\delta$  6.26 and  $\delta$  6.84, have coupling constants of 8.2 Hz and 13.7 Hz, respectively. Assignment of the remaining two doublets is questionable. A broad singlet at  $\delta$  6.62 could mask both partners for the resonances at  $\delta$  6.63 and  $\delta$  6.64. HPLC analysis of the irradiated solution resulted in three peaks, with retention times of 2.86, 2.95, and 4.19 minutes. Phenanthrene is the last component to

elute, while the two earlier peaks probably correspond to cis- and trans- $\beta$ -chlorostyrenes. However, no  $\beta$ -chlorostyrenes were isolated upon application of the product mixture to a prep TLC plate. This was not too surprising, since  $\beta$ -chlorostyrenes readily polymerize.

Another potential carbene precursor which was prepared from **22** was the chloromethyl adduct (**Scheme 41**). Again, the concurrent formation of monochloro adduct was evident in the  $^1\text{H}$

**Scheme 41**

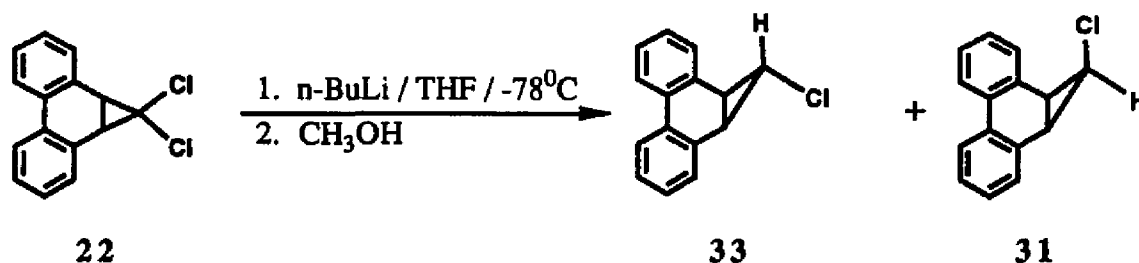


NMR spectrum. This adduct also decomposed on a silica gel column, and was, therefore, purified on florisil. White crystals were obtained in 11% yield following column chromatography. Significant resonances in the  $^1\text{H}$  NMR include a singlet at  $\delta$  1.86 (methyl protons) and a singlet at  $\delta$  2.65 (bridgehead protons). Preliminary photolysis of **32** resulted in phenanthrene formation, as monitored by HPLC and TLC. A single attempt to trap

chloromethylcarbene with cyclohexene was made. The irradiation of a pentane solution of **32** and cyclohexene was performed at 254 nm for 30 mins. By  $^1\text{H}$  NMR, the vinylic resonance at  $\delta$  5.67 corresponding to cyclohexene was gone, and several new peaks in the aliphatic region had emerged. It was, however, impossible to definitively assign peaks to the expected cycloaddition products.

The final carbene progenitor which was examined was the monochloro adduct, a product which had formed during synthesis of both the benzylchloro and chloromethyl adducts. Having obtained a single isomer during the course of these alkylations, we were surprised to obtain both the endo and exo isomers upon quenching the carbenoid with methanol (**Scheme 42**). The endo chloro isomer is selectively destroyed during column chromatography on silica gel. Attempted trapping of monochloro carbene with cyclohexene was unsuccessful. Phenanthrene was

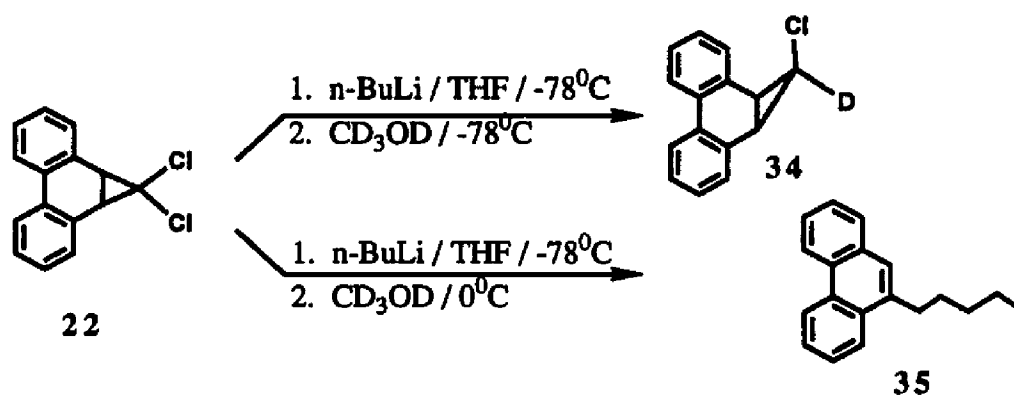
**Scheme 42**



generated during photolysis, but no trapped products were identified through high-field NMR or HPLC.

We decided to explore the stability of the carbenoid through quenching experiments at two different temperatures. Two quenching reactions were run, using deuterated methanol as the quenching agent. In one flask, CD<sub>3</sub>OD was added at -78°C, while in the other flask, quenching occurred at 0°C. The expected monodeuterated product, whose structure was confirmed by NMR and MS, was obtained at -78°C. When quenching took place at 0°C, the results were not as straightforward. <sup>1</sup>H NMR revealed resonances suggestive of a butylated product (recall that n-butyl chloride is formed during generation of the carbenoid). Resonances indicative of phenanthrene derivatives were also evident. A parent peak at m/z=248 in the mass spectrum suggested the 9-n-pentylphenanthrene structure in **Scheme 43**. The origin of this compound is unknown.

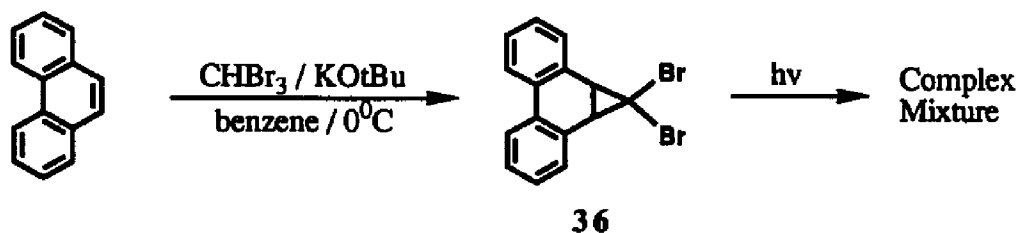
### Scheme 43



### ATTEMPTED GENERATION OF DIBROMOCARBENE

Flush with our success, we began to explore other potential photochemical carbene precursors. Our thoughts turned initially to the dibromo analogue of **22**, whose synthesis has been reported in the literature (Scheme 44).<sup>59</sup> In an effort to trap dibromocarbene, a pentane solution of **36** and cyclohexene was

### Scheme 44



irradiated at 300 nm in a Rayonet apparatus. Photolysis times were

varied (1 min., 9 min., 30 min., 60 min.), but the results were the same: a veritable plethora of photoproducts formed! A dark experiment was run in order to confirm that the products had indeed resulted from irradiation. Both HPLC and 360-MHz  $^1\text{H}$  NMR analysis clearly showed phenanthrene formation, thus implying generation of dibromocarbene. Based on the number of resonances observed in the  $^1\text{H}$  NMR spectrum, however, it is apparent that this is not a viable photochemical precursor of dibromocarbene.

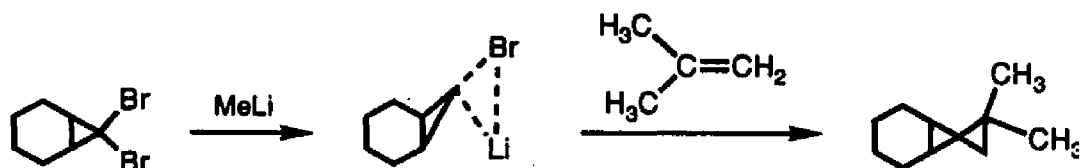
Why was dichlorocarbene cleanly generated by this method, while dibromocarbene was not? C-Br bonds are longer and weaker than C-Cl bonds, making them more susceptible to homolytic cleavage. It seems likely that C-Br cleavage occurs, thereby forming bromine radicals. The resulting product mixture would be quite complex.

#### ATTEMPTED SYNTHESIS OF CYCLOPROPYLIDENE PRECURSORS

The reaction of gem-dihalocyclopropanes with alkyllithiums provides access to allenic compounds.<sup>60</sup> When this reaction is carried out in the presence of an alkene, the resulting product

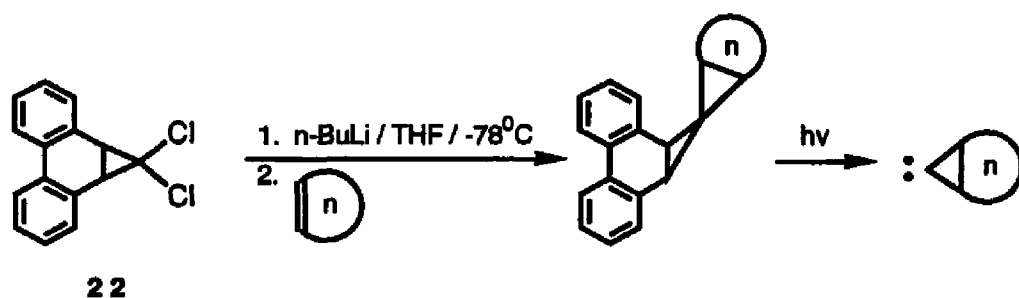
contains a spiropentane moiety (**Scheme 45**).<sup>61</sup> The spirocycle is proposed to arise from cycloaddition of the carbenoid intermediate

**Scheme 45**



to the alkene trap. Based on our success in alkylating carbenoid **22**, we attempted to form the corresponding spirocycle by trapping this intermediate with a cyclic alkene (**Scheme 46**). The ultimate goal of this project was to photochemically generate a cyclopropylidene, another type of carbene whose absolute kinetics have never been measured.<sup>62</sup>

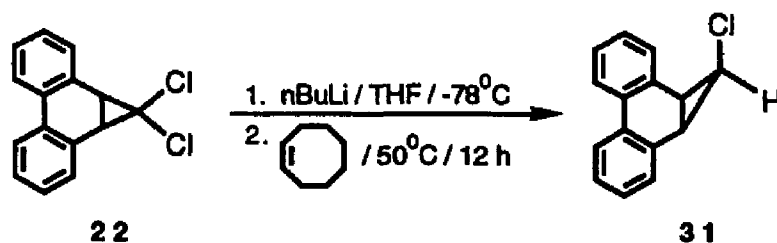
**Scheme 46**



Our initial study employed dichloroadduct **22** and cyclooctene (**Scheme 47**). The first set of conditions utilized required addition of cyclooctene to the intermediate carbenoid at -78°C,



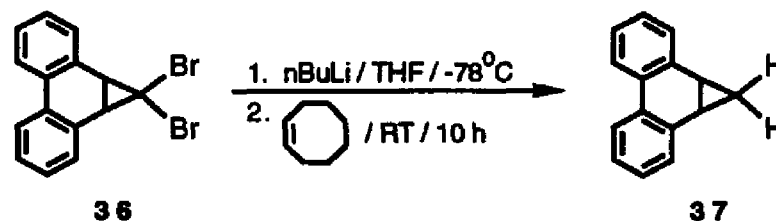
#### Scheme 47



with work-up performed when the reaction mixture reached room temperature. This protocol led primarily to formation of the monochloro adduct. No evidence for a spirocycle was observed. A second attempt was made with quenching at -78°C, followed by stirring at room temperature for 10 h. This procedure also resulted in formation of the monochloro adduct. In an attempt at brute-force chemistry, the reaction mixture was heated to 50°C for 12 hours after reaching room temperature. The reduced compound was once again the chief product observed. Clearly, the carbenoid does not react efficiently with cyclooctene.

Since many spirocycles are synthesized from bromo-lithio carbenoids,<sup>63</sup> we decided to repeat the above experiment using the dibromo carbene adduct, 36 (Scheme 48). n-Butyllithium was added to a THF solution of 36 at -78°C in order to generate the carbenoid. Cyclooctene was subsequently added, the solution warmed to room temperature, and stirring continued for an

#### Scheme 48



additional 10 hours. The crude product was purified by preparative TLC, yielding a white solid.  $^1\text{H}$  NMR analysis indicated this material to be the fully reduced adduct (37), by comparison with known spectral data.<sup>64</sup>

In the belief that a more reactive alkene might facilitate the reaction, the above sequence was repeated with cyclohexene. As before, no spirocycle seemed to have formed. The products appeared to be the partially reduced (monobromo) and fully reduced analogues. None of the pathways explored in the synthesis of a cyclopropylidene precursor proved fruitful. This synthesis remains an important goal, but will require a different synthetic method.

## CONCLUSION

The initial goal of this project was to determine if our dichlorocarbene precursor, **22**, was a suitable photochemical progenitor for use in kinetic studies. Collaboration with John Chateaufort at the University of Notre Dame was spectacularly successful, permitting the first measurement of the absolute rate constants for the reaction of dichlorocarbene with a series of alkenes. Efforts to demonstrate formation of triplet dichlorocarbene were unsuccessful. Attempts to generate dibromocarbene from the analogous dibromo precursor, **36**, were ineffectual; photolysis of this compound led to a multitude of products.

Modification of this dichloro adduct led to the synthesis of three potential photochemical precursors for benzylchlorocarbene, chloromethylcarbene, and chlorocarbene. Preliminary photolysis studies suggested formation of the corresponding carbenes. Additional trapping studies need to be implemented, however, to rigorously demonstrate carbene generation.

The dibromo adduct proved useful as the starting material in our attempts to develop a suitable photochemical precursor for

cyclopropylidene. . Despite our lack of progress in this area, the proposed route appears to be a logical approach to cyclopropylidene. Cyclopentene may prove to be a more effective trap for the intermediate carbenoid. An alternate approach, such as alkylation of the carbenoid followed by ring closure, may also provide access to the desired spirocycle.

## **CHAPTER 3**

### **SYNTHESIS OF STRAINED CYCLIC CUMULENES**

#### **INTRODUCTION**

Just how much strain can be incorporated into a molecule before it ceases to exist as an isolable entity and becomes a reactive intermediate? This question has intrigued chemists since the introduction of strain theory by von Baeyer in 1885.<sup>65</sup> von Baeyer proposed that cyclopropane and cyclobutane would be less stable than larger carbocyclic rings, due to bond angle distortion away from the ideal  $109.5^\circ$  associated with  $sp^3$  carbon hybridization. Synthesis of both the three- and four-membered rings was achieved by Perkin, working in von Baeyer's lab at the time.<sup>66</sup>

Strain is introduced into a molecule whenever a geometrical parameter, such as bond angle or bond length, deviates from the normal or "ideal" value.<sup>67</sup> Two concepts which are used to quantify the strain inherent in a molecule are strain energy (SE) and olefinic strain (OS). Strain energy is defined as the difference between the

observed heat of formation and that calculated for a hypothetical, strain-free molecule. An "unstrained" cyclopropane, for example, would have a heat of formation of -14.85 kcal/mol, obtained from the thermochemical group increment for  $\text{CH}_2$ . The enthalpy of formation of cyclopropane has been measured as 12.74 kcal/mol. The difference between these two figures, 27.5 kcal/mol, is considered to be the strain energy of cyclopropane.

The difference in strain energy between an alkene and its analogous alkane has been defined by Schleyer as olefinic strain.<sup>68</sup> This term approximates the strain which results upon incorporation of a double bond into a fully saturated system. Introduction of a double bond into a ring can increase or decrease the strain energy relative to the saturated system. The olefinic strain of cyclopropene is 28 kcal/mol, due largely to the greater bond angle compression from the normal  $120^\circ$  for an  $\text{sp}^2$  carbon. Cyclopentene, on the other hand, is less strained than cyclopentane. In this instance, introduction of the double bond decreases torsional interactions, thereby lowering the strain energy of the molecule.

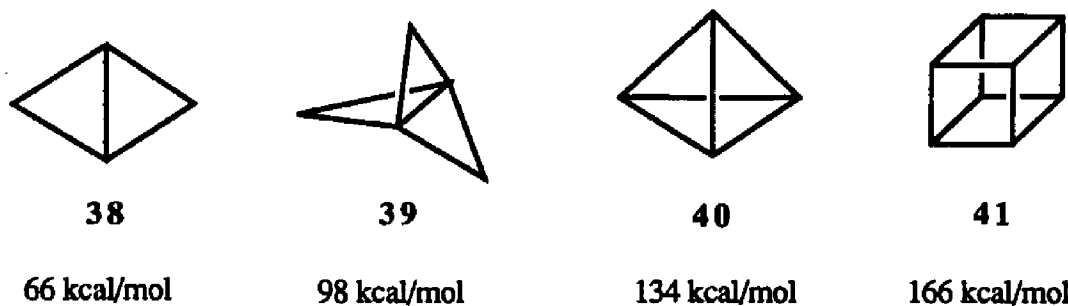
Five types of strain have been defined to describe strained molecules.<sup>67b,c</sup> Bond-angle distortion, or Baeyer strain, is the

primary source of strain in small rings and cyclic olefins. The inability of bonds to assume a staggered conformation, due to restrictions imposed by a ring, gives rise to torsional strain. Bending or twisting of a double bond introduces strain into a molecule, as does steric crowding. Finally, stretching or compressing a bond from its normal value adds to the strain energy of a compound. Each type of strain, along with selected examples, will be discussed below.

The classic example of a small, strained ring is cyclopropane, in which the bond angles are significantly compressed from the optimum tetrahedral value of  $109.5^\circ$ . To compensate for this distortion, the  $\sigma$  bonds "bend" to give an angle of approximately  $78^\circ$ , larger than the formal angle of  $60^\circ$ . These bonds are weaker than typical carbon-carbon bonds, and possess some double bond character.

Several more exotic examples of rings whose strain results from  $\sigma$ -bond distortion, are depicted in **Figure 8**, along with their estimated strain energies. [1.1.1] Propellane (**39**), first synthesized by Wiberg and Walker in 1982,<sup>69</sup> derives its strain from the inverted tetrahedral geometry imposed on the bridgehead carbon

**Figure 8**



atoms. Hybridization at the bridgehead positions approximates  $sp^2$ , thereby rendering the central bond susceptible to reaction with electrophiles.

The central bond in bicyclobutane (**38**) is also highly reactive, and has been estimated to have 40% s character.<sup>70</sup> Analysis of the microwave spectrum of bicyclobutane indicates the bridgehead carbon-carbon bond to be approximately 1.497 Å long, reflecting the large s component in this bond.<sup>71</sup>

Tetrahedrane (**40**) and cubane (**41**) are representatives of polycarbocyclic cage systems,  $(CH)_n$ . Despite the high strain energy estimated for cubane, this molecule is surprisingly stable, and remains intact up to 200°C. Several syntheses of cubane and its derivatives have been developed.<sup>72</sup> Tetrahedrane, which should enjoy a lower strain energy than cubane, has nevertheless eluded synthesis, although the tetra-*tert*-butyl derivative is known.<sup>73</sup> It

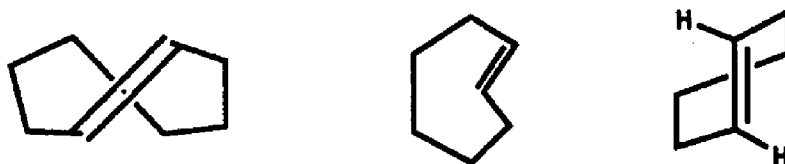


appears that the greatest barrier to isolability of tetrahedrane is the propensity of this molecule to rearrange to the bicyclobutyl diradical.

Sources of strain in cyclobutane are twofold: angle compression and torsional interactions. Bond angles are  $90^\circ$  for planar cyclobutane, however, this would result in eclipsing of all four methylene groups. Puckering of the cyclobutane ring staggers the methylene groups, but distorts the angles further to  $88^\circ$ . The compromise results in a puckered conformation of cyclobutane, which is favored over the planar conformation by 1.5 kcal/mol.

In small rings, trans double bonds are both bent and twisted (Figure 9). Trans-cyclooctene, approximately 11 kcal/mol higher

**Figure 9**

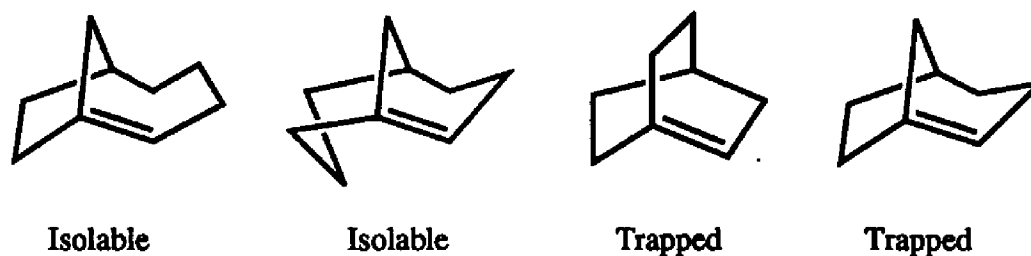


in energy than its cis counterpart, is the smallest trans-cycloalkene which has been isolated at room temperature.<sup>74</sup> Trans-cycloheptene has been produced by low-temperature photolysis of cis-cycloheptene; isomerization to the cis form occurs at  $1^\circ\text{C}$ .<sup>75</sup>

Joussot-Dubien and coworkers have presented evidence that trans-1-phenylcyclohexene is formed by photochemical cis-trans isomerization.<sup>76</sup> Computational studies suggest that trans-cyclohexene may be detectable if generated in a matrix or if coordinated with a transition metal.<sup>77</sup>

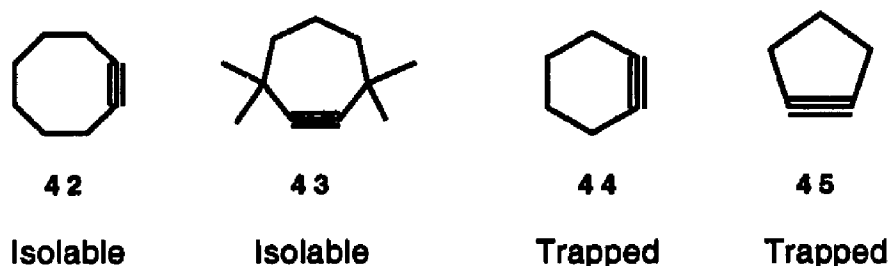
Compounds which contain bridgehead double bonds also experience  $\pi$ -bond distortion. In the nineteenth century, it was believed that a molecule possessing a bridgehead double bond could not be isolated. This was formulated as Bredt's rule, which stated that bridgehead double bonds could only be accommodated by large rings.<sup>78</sup> Numerous examples of "anti-Bredt" molecules, however, have now been reported (Figure 10), the smallest of which contain trans-cyclooctene rings. Compounds in which the trans double bond is incorporated into a smaller ring exist only as reactive intermediates.<sup>79</sup>

**Figure 10**



As with trans-cycloalkenes and bridgehead olefins, the eight-membered ring is the smallest cyclic alkyne which can be isolated (Figure 11).<sup>80</sup> Several protocols have led to generation of cycloheptyne as a transient intermediate. This strained compound is isolable as its tetramethyl derivative **43**.<sup>81</sup> Cyclohexyne (**44**) and cyclopentyne (**45**) have also been

**Figure 11**

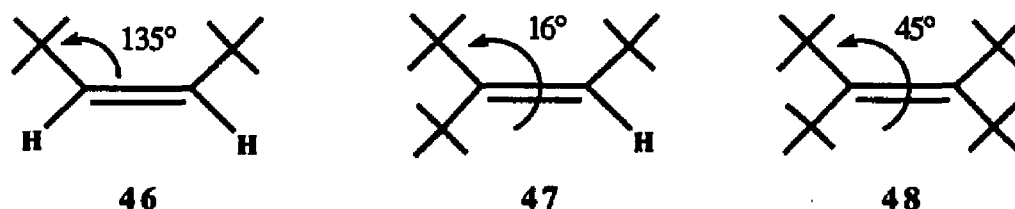


trapped, but efforts to generate cyclobutyne have been unsuccessful.<sup>82</sup> Calculations on cyclopropyne suggest that it is not an energy minimum, but rather a transition state for the degenerate rearrangement of propadienylidene.<sup>83</sup> The large amount of strain observed in the smaller cycloalkynes can be attributed to the inability of the acetylenic moiety to assume a linear conformation.

Steric crowding occurs when large, bulky groups are placed in close proximity. The series of *tert*-butyl substituted ethylenes

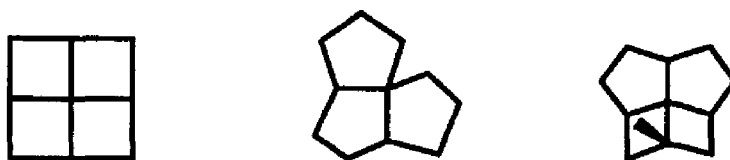
readily illustrates the effect of adding bulky substituents to the olefinic moiety (**Figure 12**). For *cis*-1,2-di-*t*-butylethylene (**46**), the bond angle opens to 135° from the normal 120° to ease steric congestion. A third *t*-butyl group (**47**) cannot be accommodated by a planar structure, which results in twisting of the double bond by an estimated 16°.84 Tetra-*t*-butylethylene (**48**) has never been synthesized; it is predicted to have a strain energy of 100 kcal/mol and a torsional angle of 45°.85

**Figure 12**



The final source of strain to be discussed is bond stretching and compression. Each type of chemical bond has a preferred length and force constant. Deviation from the norm means added strain in the molecule. Fenestranes are a class of tri- and tetra-cyclic compounds which possess a somewhat flattened central carbon atom (**Figure 13**).86 Much of the strain in these polycyclics is ascribed to shortening of the central carbon-carbon bonds to ca. 1.480 Å.

**Figure 13**



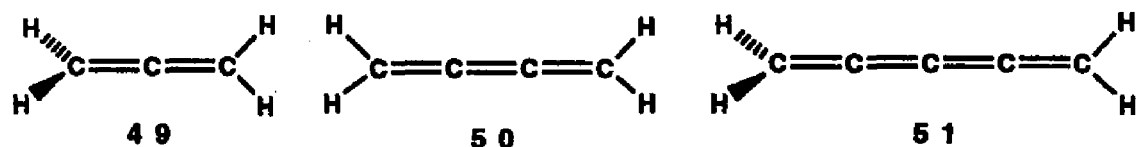
**CYCLIC BUTATRIENES:**

**SYNTHESIS AND TRAPPING OF 1,2,3-CYCLOOCTATRIENE**

**Introduction to Butatrienes**

Cumulenes are a class of hydrocarbons which contain multiple, sequential double bonds (Figure 14). Butatrienes (50) are the second member of this homologous series; their key structural

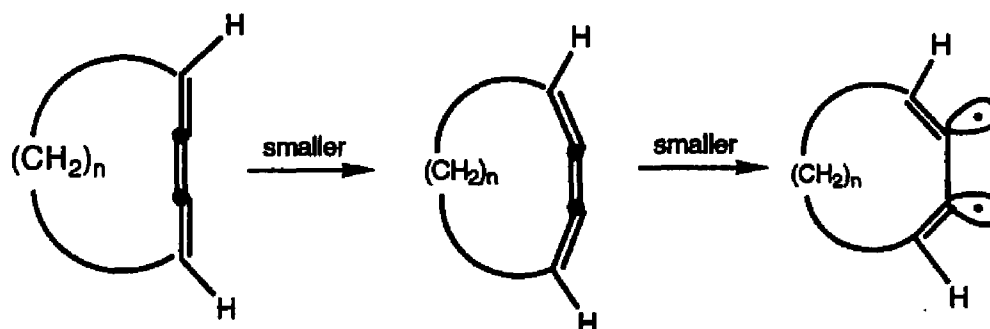
**Figure 14**



feature is the inclusion of three consecutive double bonds. Throughout the series, the central carbons are  $sp$  hybridized and, therefore, prefer a linear geometry. As the butatriene moiety is incorporated into smaller and smaller rings, the olefinic linkage

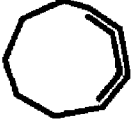
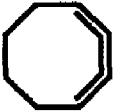
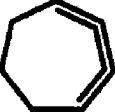


suffers from in-plane bending, resulting in rehybridization from  $sp$  towards  $sp^2$ . The smaller cyclic butatrienes are more highly strained, more reactive, and presumably more diradical in nature than their larger homologues (Scheme 49).<sup>87</sup>

**Scheme 49**



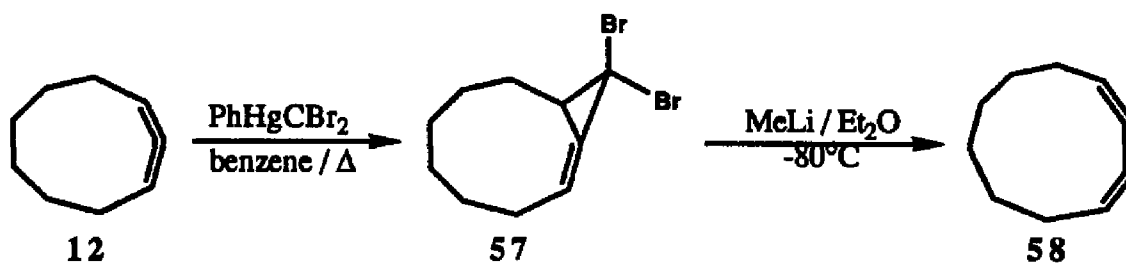
Johnson and Angus utilized MNDO calculations to predict the strain energies and bond angles for the cyclic butatriene series (Figure 15).<sup>88</sup> The predicted C1-C2-C3 bond angles decrease markedly along the series, dropping from  $162^\circ$  for 1,2,3-cyclononatriene, to  $116^\circ$  for 1,2,3-cyclopentatriene. Removal of each methylene group while descending this homologous series leads to an approximate doubling of strain energy for the resulting smaller ring.

**Figure 15**

				
<b>52</b>	<b>53</b>	<b>54</b>	<b>55</b>	<b>56</b>
Estimated Strain Energy (kcal/mol)				
5.5-8	14	31.5	60.5	130
C1-C2-C3 Bond Angle				
162°	156°	145°	132°	116°

Both the nine- and ten-membered cyclic butatrienes are isolable in solution, but polymerize upon concentration or exposure to air. Synthesis of 1,2,3-cyclodecatriene was accomplished by Moore and Ozretich in 1967. The synthesis employed standard carbenoid chemistry (Scheme 50).<sup>89</sup> Johnson and Angus

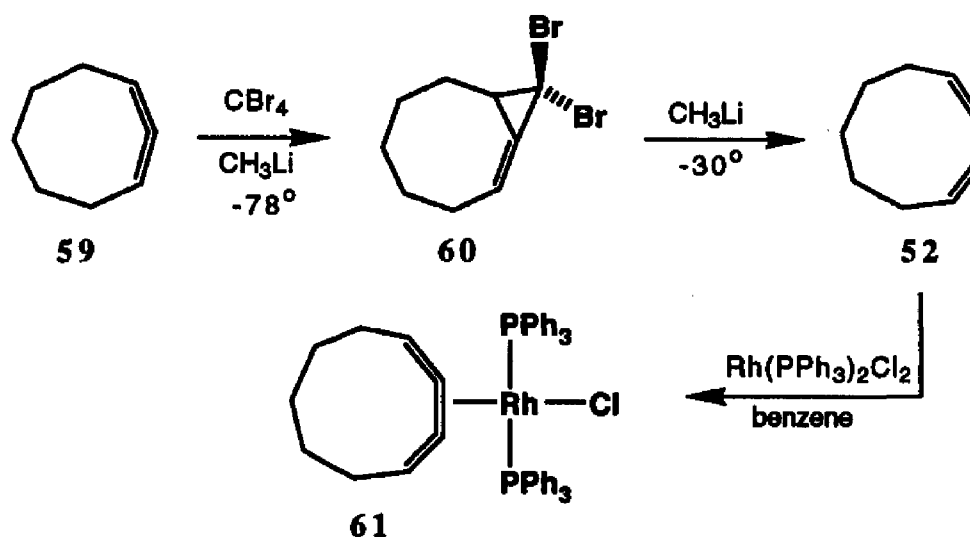
**Scheme 50**



reported the synthesis of 1,2,3-cyclononatriene in 1984, also exploiting carbenoid methodology (Scheme 51).<sup>88</sup> Cumulene 52 was

isolated as a crystalline rhodium complex (**61**), which resulted from reaction with Wilkinson's catalyst.<sup>90</sup> The butatriene bond angle is compressed to 152.2°, a larger distortion than that predicted from MNDO calculations on the parent hydrocarbon (162-165°).

**Scheme 51**

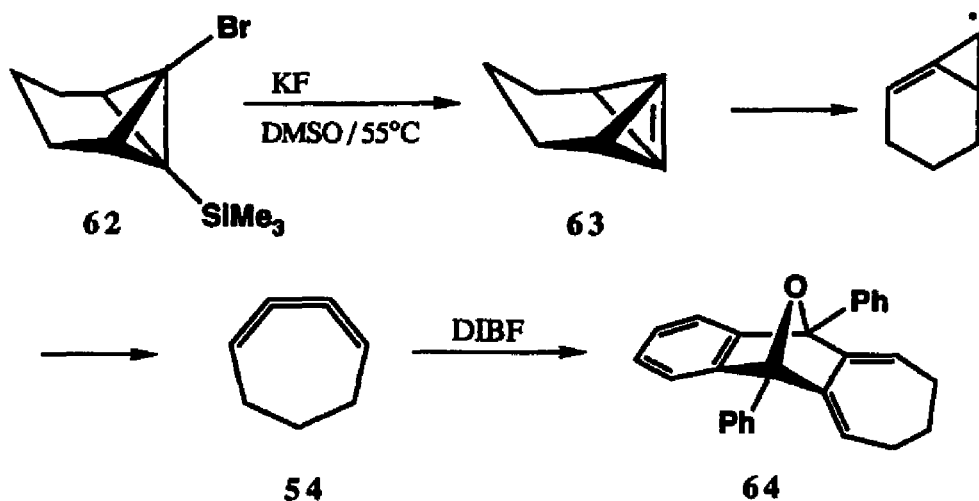


With a predicted strain energy of only 14 kcal/mol, 1,2,3-cyclooctatriene (**53**) was considered a viable synthetic target. Efforts toward its synthesis will be discussed in the next section.

An elegant experiment which led to the trapping of 1,2,3-cycloheptatriene was reported by Szeimies *et al.* in 1981 (Scheme 52).<sup>91</sup> Utilizing Chan and Massuda's fluoride-induced elimination of a  $\beta$ -halosilane to generate the strained  $\pi$  bond,<sup>92</sup> the authors treated **62** with potassium fluoride in DMSO at  $55^\circ\text{C}$  to form



**Scheme 52**



the highly strained bicyclobutene **63**. However, the isolated product was diphenylisobenzofuran adduct **64**. Similar results were obtained when 9-methoxyanthracene and anthracene were selected as traps. Szeimies proposed that the bicyclobutene intermediate rearranged to 1,2,3-cycloheptatriene, possibly through a carbenic pathway.

Encouraged by their results, Szeimies and coworkers explored the same avenue in an effort to trap 1,2,3-cyclohexatriene.<sup>93</sup> The logical precursor for this strained butatriene was bicyclic silane **65**, which was heated to  $80^\circ\text{C}$  with cesium fluoride in DMSO (Scheme 53). The only product isolated, **67**, resulted from trapping of the bicyclobutene intermediate with DIBF. No

### Scheme 53

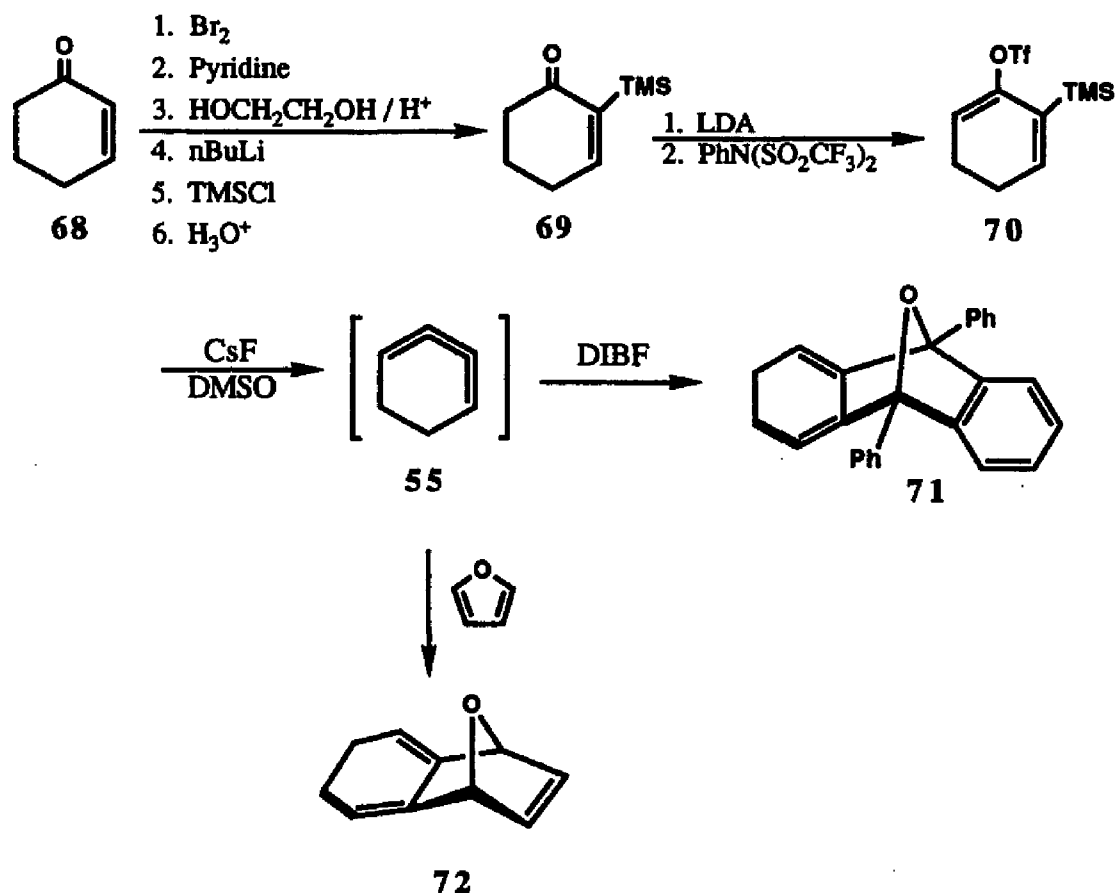


rearrangement to 1,2,3-cyclohexatriene was evident. A plausible explanation offered by the authors is that isomerization of 63 to 54 is a more exothermic reaction than the corresponding isomerization for the six-membered homologue. As noted previously, 1,2,3-cyclohexatriene is predicted to be roughly twice as strained as 1,2,3-cycloheptatriene.<sup>88</sup>

In the belief that fluoride-induced elimination of a silyl group, vicinal to a good leaving group, would permit a mild, general route to cyclic butatrienes, our group applied this protocol to the synthesis of 1,2,3-cyclohexatriene. The steps leading to the synthesis of this strained intermediate, the smallest cyclic butatriene synthesized to date, are outlined in Scheme 54.<sup>94</sup> The key intermediate in this sequence is triflate 70, formed by treatment of enone 69 with lithium diisopropylamide, and subsequent quenching with N-phenyl

triflimide.  $\beta$ -Elimination with CsF generated 1,2,3-cyclohexatriene, which was trapped by both diphenylisobenzofuran and furan.

**Scheme 54**



With a successful route to 1,2,3-cyclohexatriene developed by Shakespeare,<sup>94</sup> we chose to explore the application of this methodology to other ring sizes. Consequently, the synthesis of 1,2,3-cyclooctatriene was investigated. 1,2,3-Cyclononatriene is isolable in solution, and 1,2,3-cycloheptatriene is observable as a

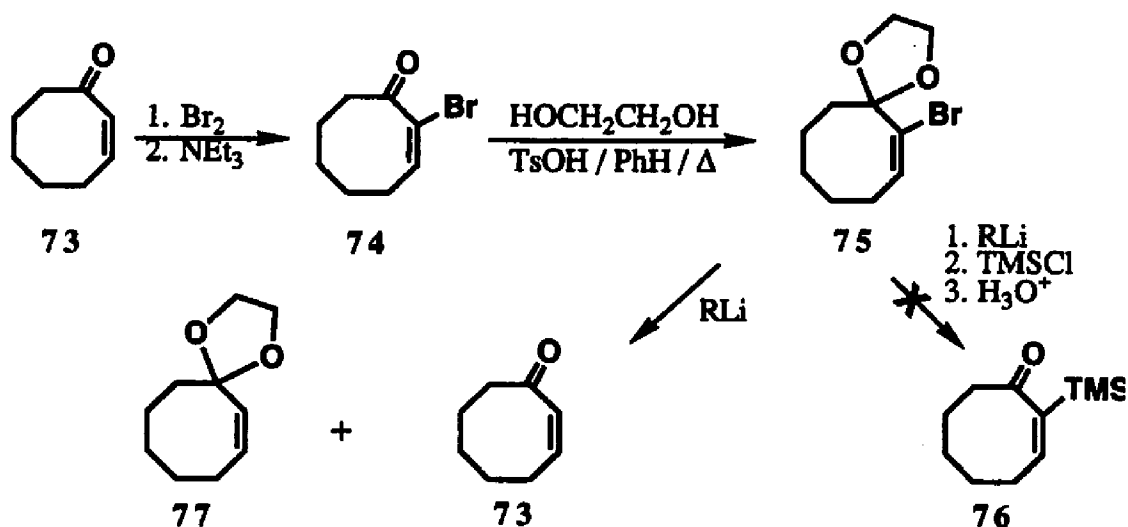
reactive intermediate; synthesis of the eight-membered cyclic butatriene would thus define the limits of isolability for this series of cumulenes.

## Results and Discussion

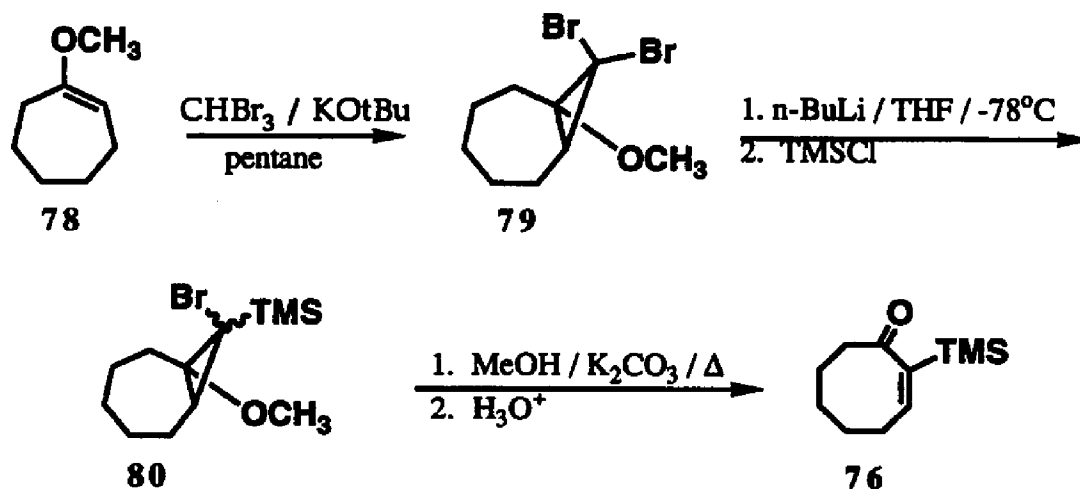
Our initial approach to 1,2,3-cyclooctatriene followed the same reaction sequence which proved so successful in the synthesis of 1,2,3-cyclohexatriene. Preliminary work by Swartz proceeded smoothly, until treatment of protected enone **75** with *n*-butyllithium (Scheme 55 ).<sup>95</sup> No silylated product (**76**) was isolated, even when *t*-butyllithium was employed. Problems with the reaction of alkylolithiums and similar compounds have been reported in the literature.<sup>96</sup> A likely scenario involves rearrangement of the initially formed anion to an allene, accompanied by ring opening of the ketal. Work-up of such an intermediate would lead to formation of both enone **73** and ketal **77**.

An alternate route to **76** is outlined in Scheme 56 . Morizawa and coworkers reported this method for the preparation of the six- and seven-membered rings.<sup>97</sup>

**Scheme 55**



**Scheme 56**

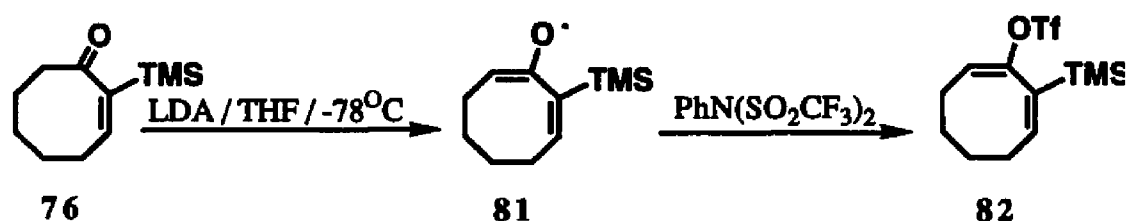


Dibromocarbene was added to 1-methoxycycloheptene 78, to give cycloadduct 79 in 39% yield after chromatography. The next four steps were conducted without isolating the intermediate

products. From previous work by Steve Swartz,<sup>95</sup> it was determined that both endo and exo trimethylsilyl isomers were formed in approximately a 1 : 2 ratio, respectively. Ring opening of intermediate **80**, followed by hydrolysis, generated the silyl-substituted enone **76** in a disappointingly low yield of 27%.

Conversion of enone **76** to triflate **82** was achieved by reaction with LDA, and subsequent quenching of the enolate with N-phenyl triflimide (Scheme 57). Purification of **82** has thus far been impossible. This compound is resistant to purification

#### Scheme 57

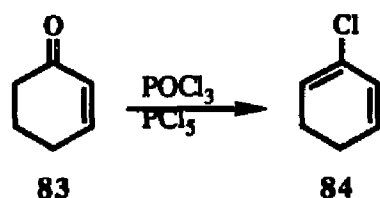


techniques: decomposition occurs on silica gel at room temperature and at  $-20^{\circ}\text{C}$ , on florisil, and upon distillation at reduced pressure. The instability of the triflate was unexpected, considering that the cyclohexadiene analogue was easily purified by column chromatography. It seems likely that decomposition occurs through loss of the triflate group to form a vinyl cation. A well-documented route to vinyl cations is via vinylic triflates.<sup>98</sup> In

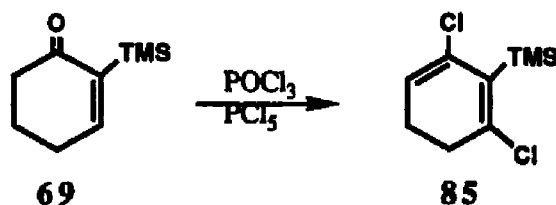
solvolysis studies on cyclooctene triflate and cyclooctadienyl triflate, Hanack and Lamparter measured the solvolysis rate of the diene to be 1,000 times faster than that of the simple alkene.<sup>99</sup> The authors believe that the eight-membered ring is flexible enough to permit stabilization of the vinyl cation through interaction with the allylic double bond. Nevertheless, it was decided to attempt a trapping experiment with impure material. Triflate **82** and cesium fluoride were stirred in DMSO, with diphenylisobenzofuran as trapping agent, at room temperature for 20 hours. As with the six-membered ring, a vinylic resonance at approximately  $\delta$  5.7 would be indicative of trapped butatriene. The 360-MHz  $^1\text{H}$  NMR of the crude product mixture was complex, but did display a triplet at  $\delta$  5.64. Purification of this sample was attempted by preparative TLC. A band containing this triplet was isolated, however, the spectral data were not consistent with the expected cycloadduct, and the structure could not be assigned from the available data.

At this juncture, we sought to synthesize a more stable precursor to the butatriene, specifically one with a less labile leaving group than triflate. Replacement of the triflate group with chlorine would afford a diene with a much poorer leaving group,

hopefully circumventing the problem of vinylic cation formation. The methodology employed was that of Axelrad, who converted cyclohexenone **83** to 2-chloro-1,3-cyclohexadiene (**84**) in 98% yield by the method shown in **Scheme 58**.<sup>100</sup> Shakespeare<sup>101</sup> reported formation of dichloride **85** when the **Scheme 58**



TMS-enone **69** was subjected to the same reaction conditions as those used by Axelrad (**Scheme 59**). Therefore, it was with **Scheme 59**

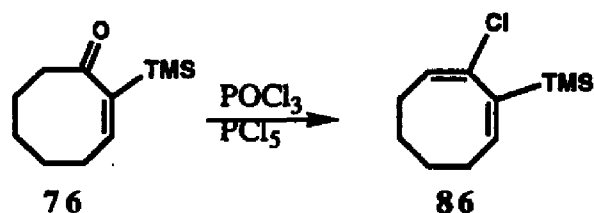


some trepidation that we treated the eight ring TMS enone **76** with equimolar amounts of  $\text{POCl}_3$  and  $\text{PCl}_5$  (**Scheme 60**). Nevertheless, the desired 1,3-diene **86** was obtained in 24% yield following purification by chromatography on alumina. The characteristic resonances in the  $^1\text{H}$  NMR spectrum for the two



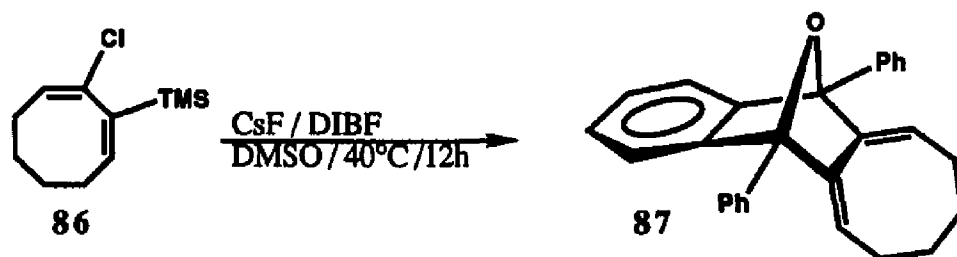
vinyllic hydrogens appear at  $\delta$  5.79 (t, 1H) and  $\delta$  6.11 (dd, 1H).

#### Scheme 60



With a pure, suitable precursor in hand, trapping experiments with diphenylisobenzofuran were attempted (Scheme 61). Since chloride is a poorer leaving group than triflate, the reaction was much more sluggish than that for the six-membered ring. After stirring at room temperature for 18 hours, a small triplet at  $\delta$  5.65 was evident in the  $^1\text{H}$  NMR, but the bulk of the reaction mixture was obviously starting material. An additional 19 hours of stirring gave more of the adduct, although a significant amount of starting

#### Scheme 61



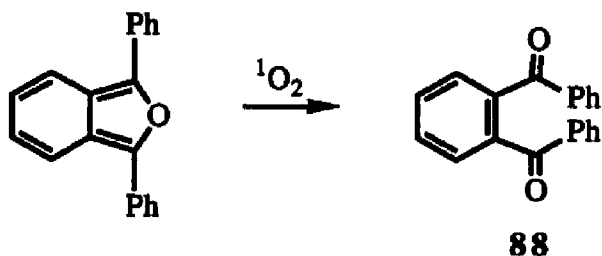
material remained. Finally, after 12 hours of heating at  $40^\circ\text{C}$ , the reaction had gone nearly to completion, and was subsequently

worked up. The desired product was isolated as a white solid in 7% yield by preparative TLC, and initially characterized through its  $^1\text{H}$  and  $^{13}\text{C}$  spectra. Pertinent resonances include a triplet at  $\delta$  5.65 (vinylic protons) and a multiplet at  $\delta$  2.22 (allylic protons). The  $^{13}\text{C}$  spectrum displayed 12 resonances, consistent with the expected  $\text{C}_s$  symmetry of the molecule. The parent peak of the molecule was evident at  $m/z$  376 in the mass spectrum, consistent with a molecular formula of  $\text{C}_{28}\text{H}_{24}\text{O}$ . These data securely characterized the structure as adduct **87**.

A control experiment was performed in which diene **86** was heated with DIBF in DMSO in the absence of cesium fluoride. This was to ensure that the observed adduct was the result of fluoride-induced elimination, rather than the consequence of a reaction between the starting diene and the trap itself. No reaction was detected between starting material and trap; in fact, the unreacted starting material was recovered and used in a subsequent trapping experiment. Interestingly, if air was not rigorously excluded from the reaction vessel, diphenylisobenzofuran was found to react with singlet oxygen to form 1,2-dibenzoylbenzene **88** (Scheme 62). DIBF

is frequently employed as a trap for singlet oxygen.<sup>102</sup>

**Scheme 62**



With adduct 87 securely characterized, we next turned to the question of isolability of 1,2,3-cyclooctatriene. Both 1,2,3-cyclodecatriene and 1,2,3-cyclononatriene are isolable in solution, giving rise to a characteristic triplet at approximately  $\delta$  5.58.<sup>88</sup> 1,2,3-Cyclooctatriene would be expected to display a similar resonance in the proton spectrum. Diene 86 (5.1 mg) and CsF (12.3 mg) were combined in an NMR tube with DMSO- $d_6$ . The solution was purged with nitrogen, and heated in a closed tube at 45°C. The spectrum of the mixture was recorded at various intervals; at no time during 37 hours of heating was a resonance assignable to the butatriene observed. The vinylic peaks corresponding to the starting material decreased in size, and new peaks in the olefinic region were apparent; however, these were further downfield than would be expected for the butatriene and

could not be distinguished as a triplet.

It is not surprising that the butatriene could not be directly observed. The highly strained intermediate would not be expected to survive heating at 45°C for a prolonged period. This fragile species would have a better chance of being detected under milder reaction conditions. A precursor containing a leaving group intermediate in reactivity between the triflate and chloride substituent might be ideal.

In conclusion, 1,2,3-cyclooctatriene has been generated for the first time by reaction of diene **86** with cesium fluoride. An adduct of **53** with diphenylisobenzofuran has been characterized.

## **CYCLIC ALLENES**

### **INTRODUCTION**

Allenenes contain two consecutive double bonds and are the next smaller homologue in the cumulene series. The central carbon atom is sp-hybridized, thus favoring a linear geometry with orthogonal substituents. Placement of the allenic moiety within a small ring bends the  $\pi$ -bonds away from linearity, while simultaneously

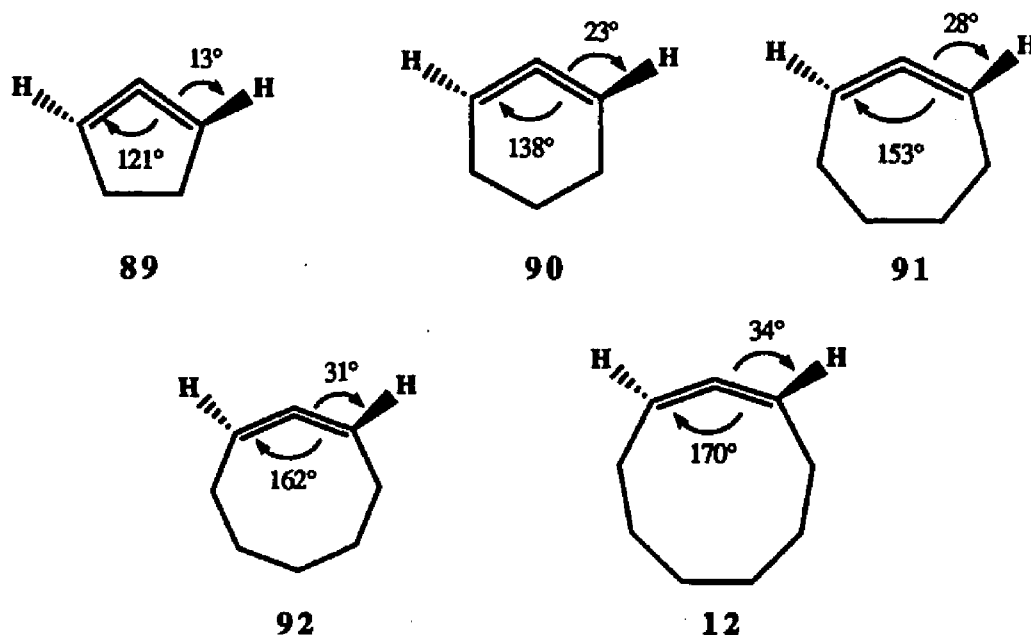
twisting the substituents towards planarity. As ring size decreases, the geometric deformation and strain increase.

Rings of ten carbon atoms or more can accommodate an allene without strain; for smaller rings, some geometric deformation is unavoidable. Figure 16 illustrates the C<sub>5</sub>-C<sub>9</sub> series of cyclic allenes, along with their bending angles and out-of-plane torsional angles, as determined from MNDO calculations.<sup>103</sup> Strain estimates increase with decreasing ring size, ranging from 41 kcal/mol for 8 **9** to 14 kcal/mol for **92**.

1,2-Cyclononadiene (**12**) is the smallest, unsubstituted cyclic allene which can be isolated. This compound is readily prepared on a large scale via the Skattebol procedure (Scheme 9, Chapter 1).<sup>104</sup> This allene is stable at room temperature, but dimerizes upon heating. The allenic moiety is predicted to be bent approximately 10° from linearity.

Unsubstituted 1,2-cyclooctadiene dimerizes readily at room temperature, however, NMR and IR data have been obtained for this strained allene at low temperatures.<sup>105</sup> Addition of a substituent to 1,2-cyclooctadiene enhances its stability. Dimerization of 1-methyl-1,2-cyclooctadiene occurs in 10-15 min at room temperature.<sup>106</sup> The

**Figure 16**

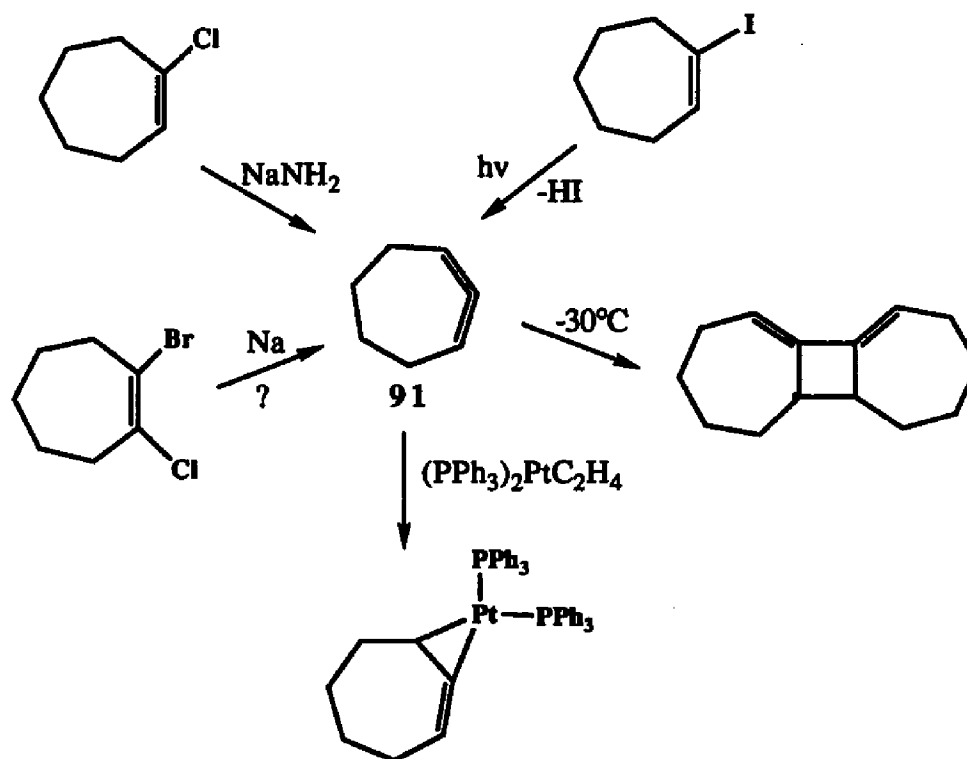


only isolable eight-ring allene is 1- *tert*-butyl-1,2-cyclooctadiene, which can even be purified by gas chromatography.<sup>107</sup> The bulky *t*-butyl group clearly prevents dimerization of the allene.

Several routes to 1,2-cycloheptadiene (**91**) have been reported in the literature (Scheme 63).<sup>87</sup> This allene is too labile to be isolated or detected spectroscopically, but has been trapped as an iron complex.<sup>108</sup> X-ray crystallography of this complex revealed an allenic bending angle of 138.1°, smaller than the predicted angle of 153° for the parent allene.

The smallest allene which has been prepared to date is 1,2-cyclohexadiene (**90**), which has been generated by a variety of

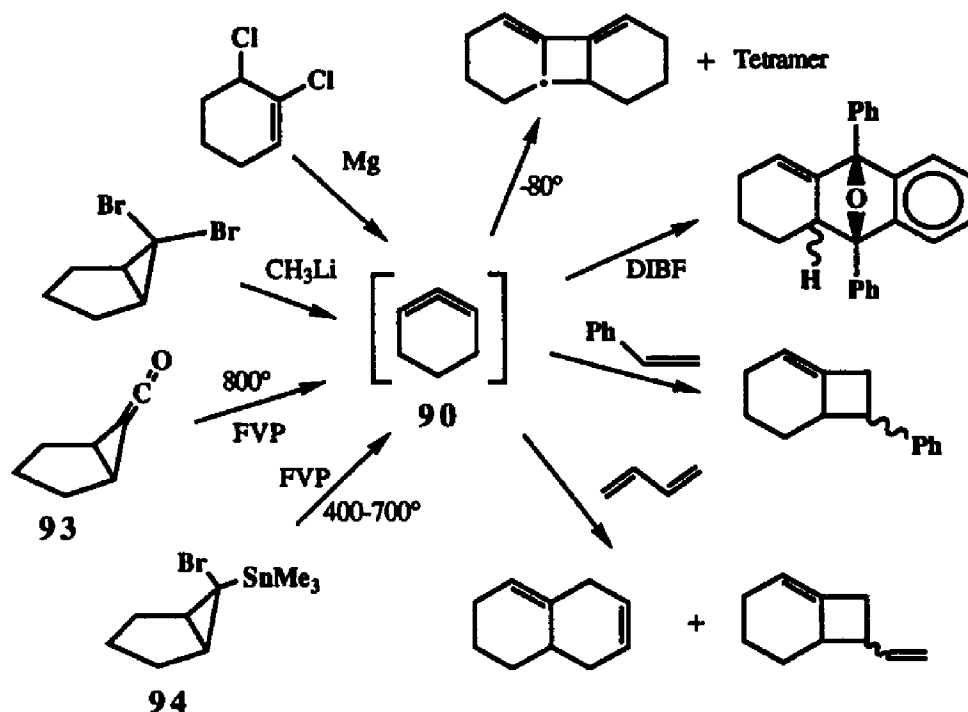
**Scheme 63**



methods (Scheme 64).<sup>87</sup> The  $\pi$ -bonds are predicted to deviate from linearity by about  $40^\circ$ ; this is accompanied by a  $23^\circ$  twisting of the allenic protons out of plane. IR absorptions for cryogenic matrix isolated 90 have been reported by two separate groups. Ketene 93 was pyrolyzed to generate the allene, which was trapped in an argon matrix at 11K by Wentrup and coworkers.<sup>109</sup> They observed an IR absorption at  $1886\text{ cm}^{-1}$ , which they attributed to 1,2-cyclohexadiene. Runge and Sander pyrolyzed precursor 94 at  $500^\circ\text{C}$ , producing an intermediate with an IR absorption of  $1829$

cm<sup>-1</sup>.<sup>110</sup> It is not clear why these two studies are not in agreement. MNDO calculations predict the IR absorption should occur at 1850 cm<sup>-1</sup> for 1,2-cyclohexadiene.

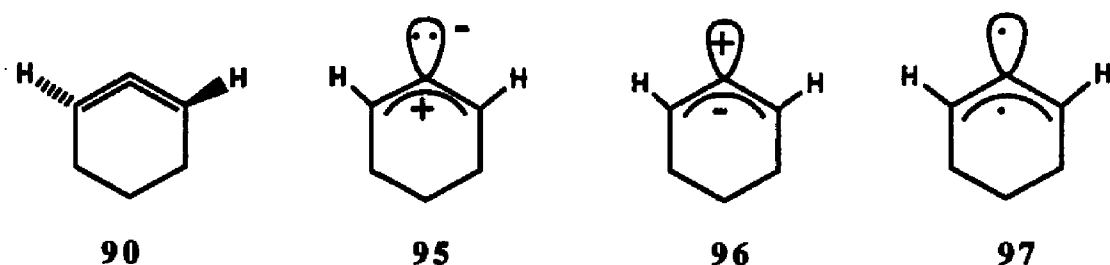
**Scheme 64**



Four possible electronic structures have been considered for the ground state of 1,2-cyclohexadiene (Figure 17). A planar intermediate, described as either a diradical (97) or zwitterion (95 or 96), was considered possible, as was a chiral species (90), in which the  $\pi$  bonds are severely distorted. Support for a chiral structure has been provided by both experimental and



**Figure 17**



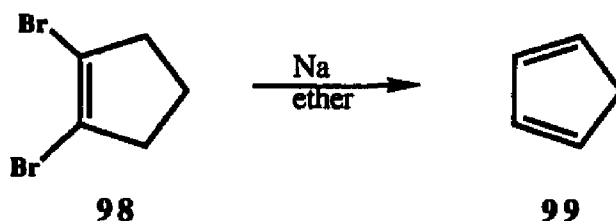
computational chemistry. An ab initio study concluded that chiral intermediate **90** was 15-25 kcal/mol lower in energy than diradical **97**.<sup>103</sup> Furthermore, optically active 1,2-cyclohexadiene was prepared by Balci and Jones, and subsequently trapped to yield optically active cycloadducts.<sup>111</sup>

Progress Toward the Synthesis of 1,2-Cyclopentadiene  
and 1-Phenyl-1,2-Cyclopentadiene

Introduction

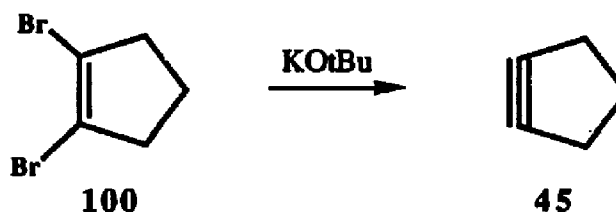
Favorski first attempted the synthesis of 1,2-cyclopentadiene in 1935. Reaction of dibromide **98** with sodium yielded 1,3-cyclopentadiene, rather than the expected allene (**Scheme 65**).<sup>112</sup> Dehydrohalogenation of 1-bromo-cyclopentene was later explored by Wittig and Heyn. Although 1,2-cyclopentadiene was not synthesized using this procedure, the smallest cyclic alkyne

### Scheme 65



known, cyclopentyne, was trapped following this protocol (Scheme 66).<sup>113</sup>

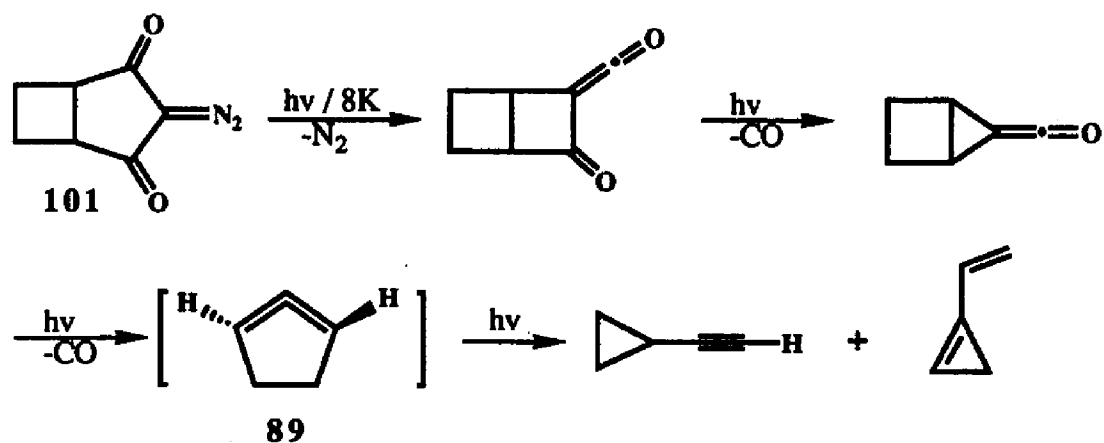
### Scheme 66



Chapman proposed the formation of 1,2-cyclopentadiene as an intermediate during photolysis of diazodiketone 101 (Scheme 67).<sup>114</sup> The allene was postulated as an intermediate based upon the products obtained, which were envisioned as arising via a 1,3-sigmatropic shift from 89. The intermediate was too short-lived to permit spectroscopic detection.

Computational chemistry (MNDO) predicts a chiral structure for this allene, which should lie 4.9 kcal/mol below the planar diradical intermediate. 1,2-Cyclopentadiene is further expected to

### Scheme 67

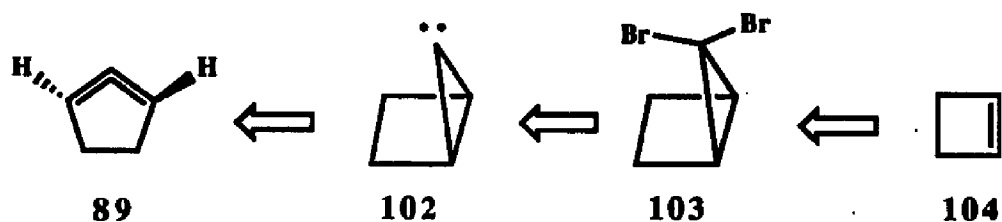


have a bending angle of  $121^\circ$ , and a torsional angle of  $21^\circ$  for the allenic hydrogens. Higher level ab initio calculations, currently in progress, give similar results.

### Results and Discussion

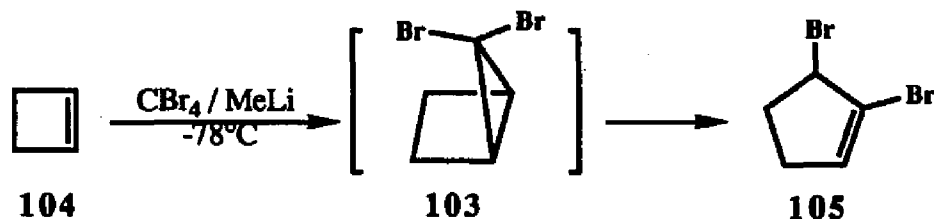
The obvious approach to 1,2-cyclopentadiene is via cyclopropylidene **102**. In principle, this can be prepared by treating dibromo adduct **103** with methyllithium at low temperature (Scheme 68). This route was explored by William Shakespeare,

### Scheme 68



whose doctoral dissertation contains pertinent experimental details.<sup>101</sup> Addition of dibromocarbene to cyclobutene at  $-78^{\circ}\text{C}$  should produce dibromocyclopropane adduct **103**. Reaction of this labile compound *in situ* with methyllithium was expected to give the elusive 1,2-cyclopentadiene. What was observed, however, was facile rearrangement of the presumably formed dibromo intermediate (**103**) to 1,5-dibromo-1-cyclopentene (**105**) (Scheme 69). Numerous variations of the reaction conditions were also unsuccessful in leading to the desired allene. It is apparent that **103** rearranges to the more stable dibromide **105**, even at  $-78^{\circ}\text{C}$ , an unexpected result in light of the fact that the analogous precursor to the six-membered allene can be distilled at  $60^{\circ}\text{C}$  under reduced pressure.

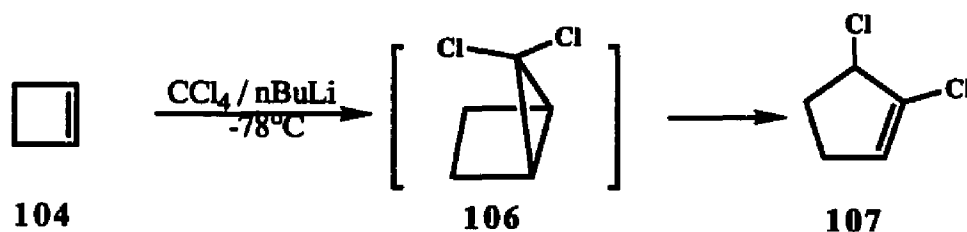
**Scheme 69**



Since dichlorocyclopropanes are less likely to ring open than dibromocyclopropanes, the above reaction sequence was performed on dichloro analogue **106** (Scheme 70). The results were

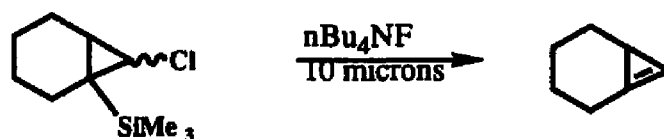
the same, however; rearrangement to 1,5-dichloro-1-cyclopentene occurred at  $-78^{\circ}\text{C}$ , and no evidence for the synthesis of 1,2-cyclopentadiene was noted.

**Scheme 70**



Since the standard carbenoid route to strained allenes failed in the synthesis of **89**, alternative methods were explored. We turned again to fluoride-induced elimination of a  $\beta$ -halosilane, an approach which has enjoyed much success in the synthesis of strained alkenes. Billups has employed fluoride columns to effect elimination, leading to strained cyclopropenes (Scheme 71).<sup>115</sup>

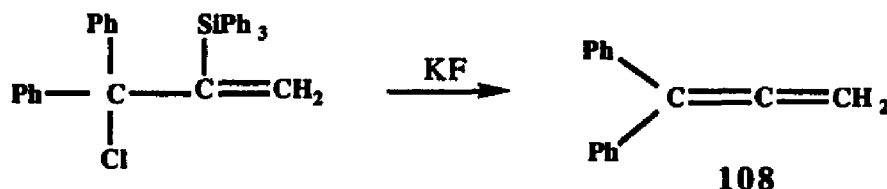
**Scheme 71**



As early as 1974, the fluoride elimination approach was applied to the synthesis of diphenylallene (**108**) by Chan and coworkers (Scheme 72), and later extended to the synthesis of other

substituted allenes.<sup>116</sup> The attractiveness of this method lies in the mild conditions employed, which allow other functional groups to be present on the molecule.

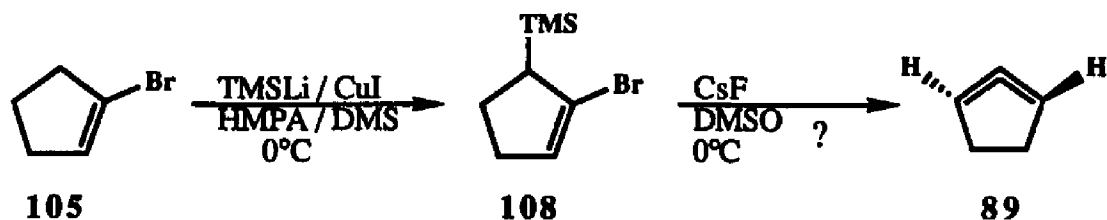
**Scheme 72**



Synthesis of the logical precursor to 1,2-cyclopentadiene, previously described in the literature,<sup>117</sup> is depicted in **Scheme 73**, and was carried out by Shakespeare. Reaction of **108** with cesium fluoride in DMSO, in the presence of diphenylisobenzofuran as trap, yielded no identifiable products. Although <sup>1</sup>H NMR showed the starting material to be gone, the only compound isolated from chromatography was DIBF.

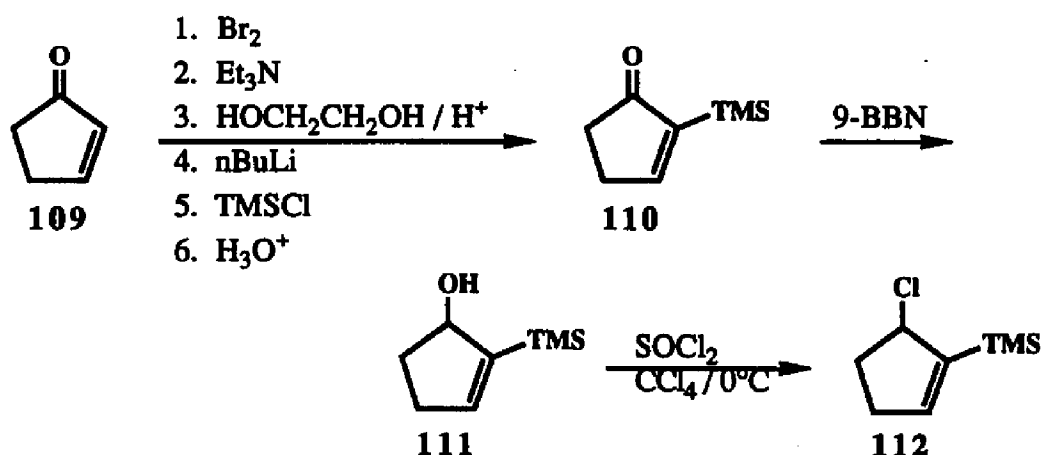
We next considered a precursor in which the halo and silyl groups have switched positions. Synthesis of this starting material is outlined in **Scheme 74**. A six-step sequence, identical to that successfully applied to the synthesis of the six-membered ring, was used to generate TMS-enone **110**. The ketone was reduced using 9-BBN, to give the allylic alcohol in 56% yield. Treatment of

### Scheme 73



111 with thionyl chloride in  $\text{CCl}_4$  at  $0^\circ\text{C}$  afforded chloride 112 as a brownish oil in 65% yield. Before attempting the elimination step, the stability of 112 was tested in  $\text{DMSO-d}_6$ . Typically,

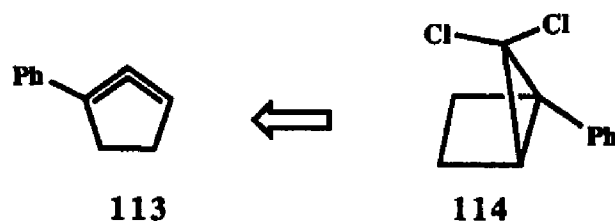
### Scheme 74



fluoride-induced  $\beta$ -elimination reactions are conducted in DMSO, although other polar solvents have been utilized.<sup>118</sup> A polar solvent is conducive to the ionic character of this reaction. Unfortunately, 112 decomposed in DMSO, presumably through heterolysis; this would generate a cation which is both allylic and  $\beta$ -silyl, and thus highly stabilized. The chloro compound was next dissolved in a

slightly less polar solvent, DMF-d<sub>7</sub>. While the severe decomposition apparent in DMSO was not seen, the <sup>1</sup>H and <sup>13</sup>C NMR spectra were not consistent with the structure of **112**, and suggested that rearrangement had occurred. The key obstacle to overcome in this route is stability of the diene precursor in a solvent suitably polar for the elimination step. This avenue was not explored further at this time, however, because an alternate path to a substituted 1,2-cyclopentadiene was apparent.

A report that 1-phenyl-5,5-dichlorobicyclo [2.1.0] pentane (**114**) is stable at room temperature was presented by E. Magyar at the 1991 Northeast Regional Meeting of the American Chemical Society.<sup>119</sup> We viewed compound **114** as a likely precursor of 1-phenyl-1,2-cyclopentadiene (**113**) (Scheme 75). If this report was correct, then adduct **114** enjoys stability not seen in the Scheme 75

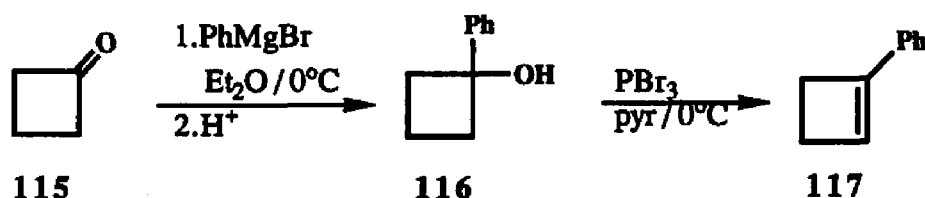


aforementioned dichloro- and dibromo-carbene adducts of cyclobutene. Consequently, the synthesis of **114**, the first two



steps of which are outlined in **Scheme 76**, was undertaken. 1-Phenylcyclobutanol (**116**) was synthesized in 96% yield by reacting cyclobutanone with phenylmagnesium bromide. Dehydration of the alcohol proved problematic. Bulb-to-bulb distillation of the alcohol with a catalytic amount of p-toluenesulfonic acid effected dehydration,<sup>120</sup> but the yield of the alkene obtained was a disappointingly low 17%. An alternate synthesis required stirring alcohol **116** at 0°C with pyridine and PBr<sub>3</sub>, and produced **117** in comparable yield.

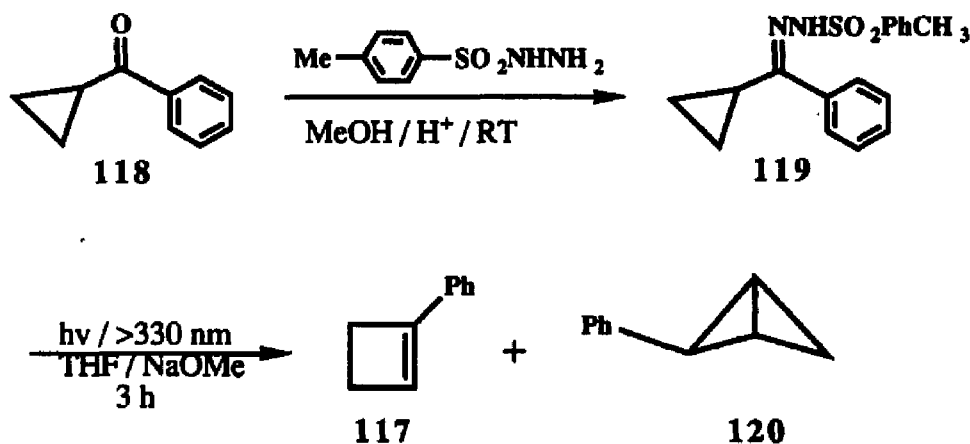
**Scheme 76**



Since neither of these methods gave a high yield of **117**, and since the starting material was rather costly, one other approach to the alkene was explored (**Scheme 77**).<sup>121</sup> The key step in this sequence involves irradiation of tosylhydrazone **119** to form an intermediate carbene, which leads to 1-phenylcyclobutene upon rearrangement. Conversion of ketone **118** to the tosylhydrazone proceeded in 75% yield, obtained as a pure white solid following

filtration.<sup>122</sup> Irradiation of **119** with sodium methoxide in THF produced the expected alkene **117**, along with phenylbicyclobutane (**120**), and an unknown carbonyl compound (<sup>1</sup>H NMR, d 9.92; IR, 1695 cm<sup>-1</sup>). Since the reaction did not proceed cleanly, it was not considered a viable route to 1-phenylcyclobutene.

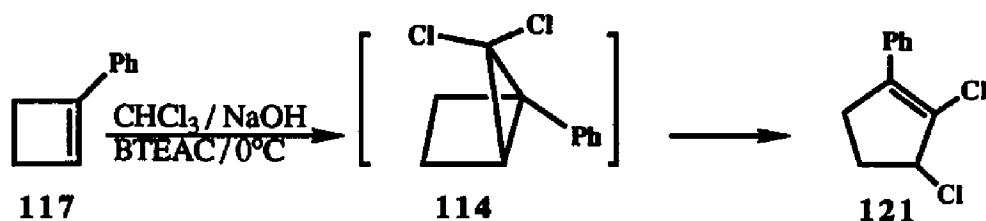
Addition of dichlorocarbene to olefin **117** was carried out using the classic phase-transfer catalysis method (Scheme 78). The reaction and work-up were conducted at 0°C because the product was expected to be quite fragile. However, contrary to the Scheme 77



previous report, the <sup>1</sup>H NMR of this sample did not suggest formation of the dichlorocarbene adduct, but rather a rearranged product (**121**), analogous to that seen for the unsubstituted cyclobutene.<sup>101</sup> This was confirmed when the NMR sample was allowed to stand

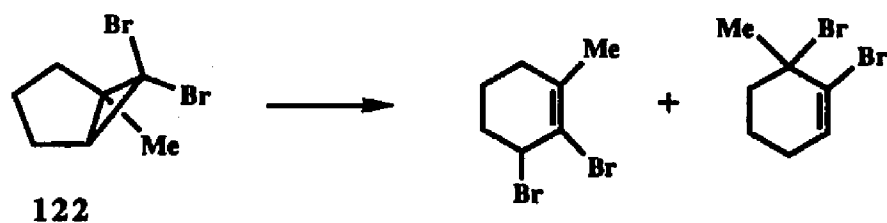
overnight at room temperature; no change in the spectrum was observed. Since then, the authors have reported difficulty in repeating their results.<sup>123</sup>

#### Scheme 78



The instability of 114 should not be surprising, since substitution has been shown to facilitate rearrangement. Christl and coworkers, for example, have reported rearrangement of 122 (Scheme 79).<sup>124</sup> In contrast, the parent compound can be distilled under reduced pressure at  $60^\circ\text{C}$ .

#### Scheme 79



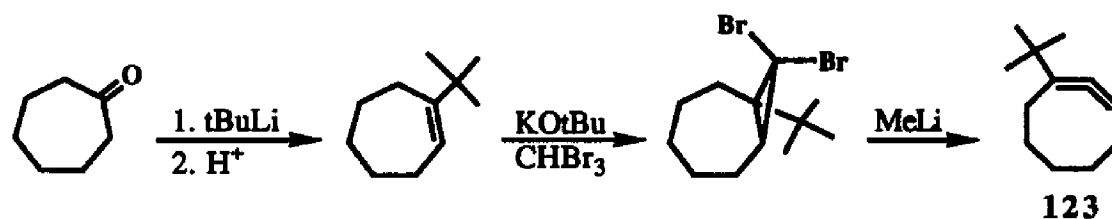
In conclusion, neither 1,2-cyclopentadiene nor 1-phenyl-1,2-cyclopentadiene has yet been synthesized. Nevertheless, the silyl elimination route to 1,2-cyclopentadiene appears promising. The precursor to this strained molecule is stable; suitable reaction

conditions for the elimination step remain to be determined. Synthesis of the phenyl substituted cyclic allene remains in doubt, due to our inability to isolate a stable precursor. We conclude that reports on the stability of adduct **114** may be in error.

#### Attempted Synthesis of 1-*t*-Butyl-1,2-cycloheptadiene

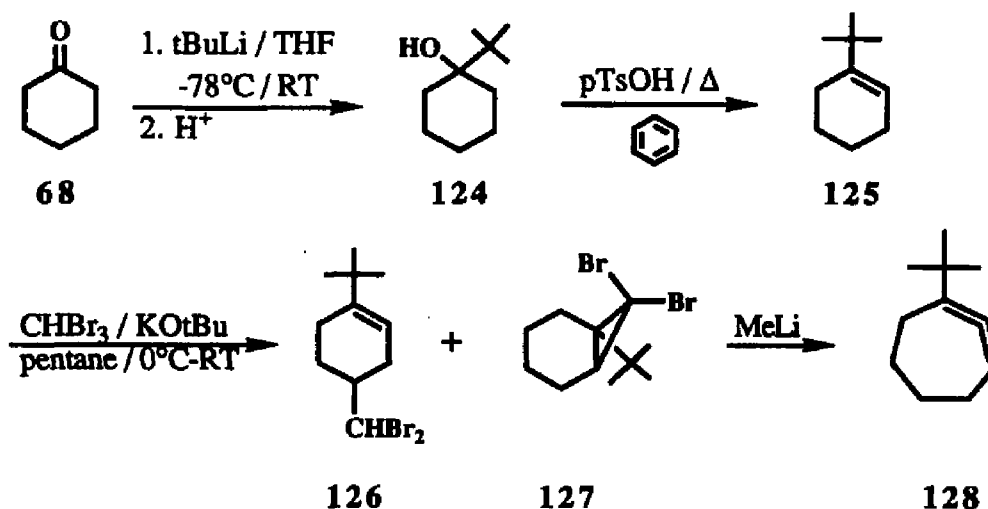
A synthetic approach to 1-*t*-butyl-1,2-cycloheptadiene was briefly explored. 1-*t*-Butyl-1,2-cyclooctadiene (**123**), whose synthesis is shown in **Scheme 80**, is the smallest substituted cyclic allene which can be isolated.<sup>125</sup> The bulkiness of the *t*-butyl group retards dimerization, facilitating isolation of the cyclic allene.

**Scheme 80**



The proposed route to **128** is outlined in **Scheme 81**. Addition of *t*-butyllithium to cyclohexanone in THF at -78°C produced alcohol **124** in 61% yield, based on recovered starting material. This compound had the delightful aroma of decaying

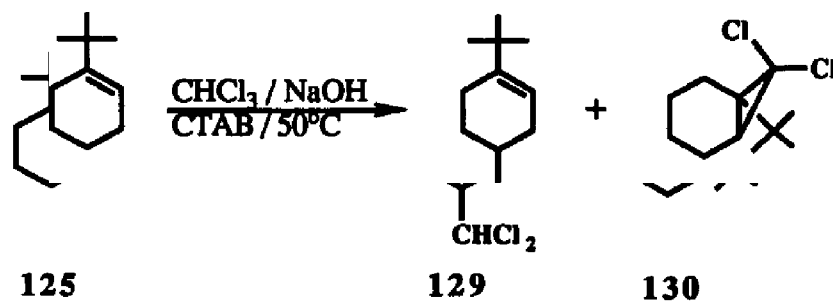
**Scheme 81**



grass. Dehydration of the alcohol was accomplished by heating the alcohol in benzene with  $p$ -toluenesulfonic acid. Addition of dibromocarbene to alkene 125, however, was not as straightforward as anticipated. From both the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, it appeared that dibromocarbene had both inserted into a C-H bond (126) and added across the double bond to form the cyclopropanation product (127). Resonances indicative of the insertion product appeared at  $\delta$  5.44 (olefinic proton) and  $\delta$  5.72 ( $\text{CHCl}_2$ ).

Dichlorocarbene was also added to 1- $t$ -butylcyclohexene (Scheme 82). Spectra for this product mixture were virtually identical with those obtained in the dibromocarbene case. In

**Scheme 82**

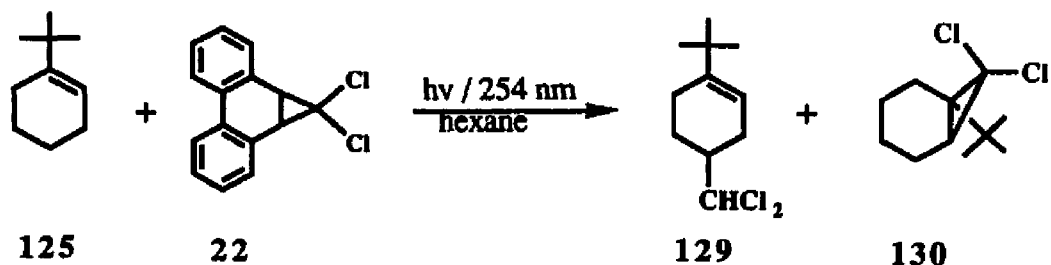


particular, the  $^{13}\text{C}$  NMR spectrum clearly showed the presence of both products. Vinylic resonances for the insertion product occurred at 116 ppm and 151 ppm, a slight shift from the resonances of the starting alkene, found at 117 ppm and 146 ppm. It appeared that the cyclopropane product was slightly favored over the insertion product. Low-temperature florisil chromatography was attempted to purify the cycloadducts, but no separation was observed at  $-20^\circ\text{C}$ .

A final attempt to synthesize 1-*t*-butylcycloheptene was through addition of photochemically generated dichlorocarbene to the alkene **125** (Scheme 83).<sup>126</sup> The reagents were irradiated in the Rayonet at 254 nm for 3 hours, and the  $^1\text{H}$  NMR spectrum of the product mixture was in good agreement with that obtained from the previous addition of dichlorocarbene.

Due to time constraints, this project was not pursued further. It seems that the limited flexibility of the six-membered ring,

### Scheme 83



coupled with the bulkiness of the *t*-butyl group, makes insertion of the carbene into a C-H bond competitive with addition across the double bond. In future work, the synthesis of 1-*t*-butyl-1,2-cycloheptadiene may be accomplished either by separating the cycloaddition and insertion isomers, or through development of an entirely different precursor.

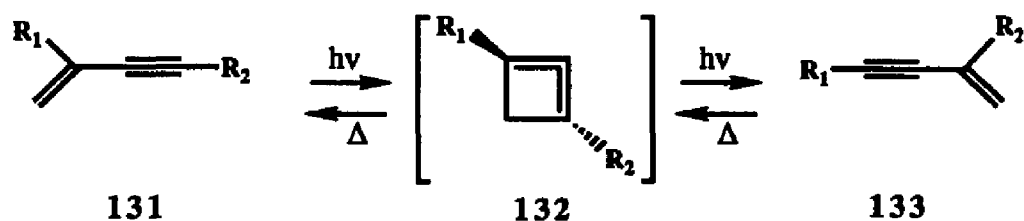
### Computational Studies on 1,2-Cyclobutadiene

#### Introduction

Because of our interest in strained, cyclic allenes, we decided to investigate the case of 1,2-cyclobutadiene. Since 1,2-cyclopentadiene has so far resisted detection, how could a smaller, more highly strained allene be identified? To explore this question, we chose to investigate the degenerate rearrangement of vinylacetylene. In principle, this might photocyclize to

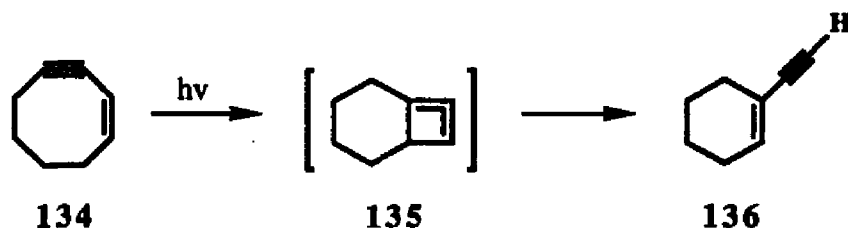
1,2-cyclobutadiene, which would then thermally ring open as depicted in **Scheme 84**. If the reaction occurs as predicted, then  $R_1$  and  $R_2$  should change positions. All of the experimental work performed on this project was conducted by Manli Zheng.<sup>127</sup>

**Scheme 84**



A single report of a photochemical enyne rearrangement has appeared in the literature. Meier and König irradiated a pentane solution of 1-cycloocten-3-yne (134) in a Hanovia apparatus to produce 1-ethynylcyclohexene (136) (**Scheme 85**).<sup>128</sup> A potential intermediate in the reaction pathway is a 1,2-cyclobutadiene structure (135), arising from an electrocyclization reaction.

**Scheme 85**

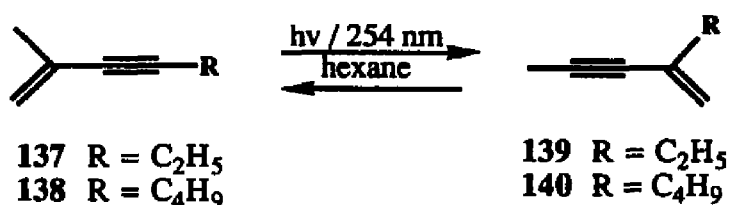


The reactions studied are depicted in **Scheme 86**. Dilute



hexane solutions of the starting enynes were irradiated through quartz at 254 nm for 37 hours. The photoproducts were characterized by spectroscopy and independent synthesis. Irradiation of enynes **137** and **138** does indeed lead to clean photoequilibration with **139** and **140**, respectively; this appears to be a very general photoreaction.

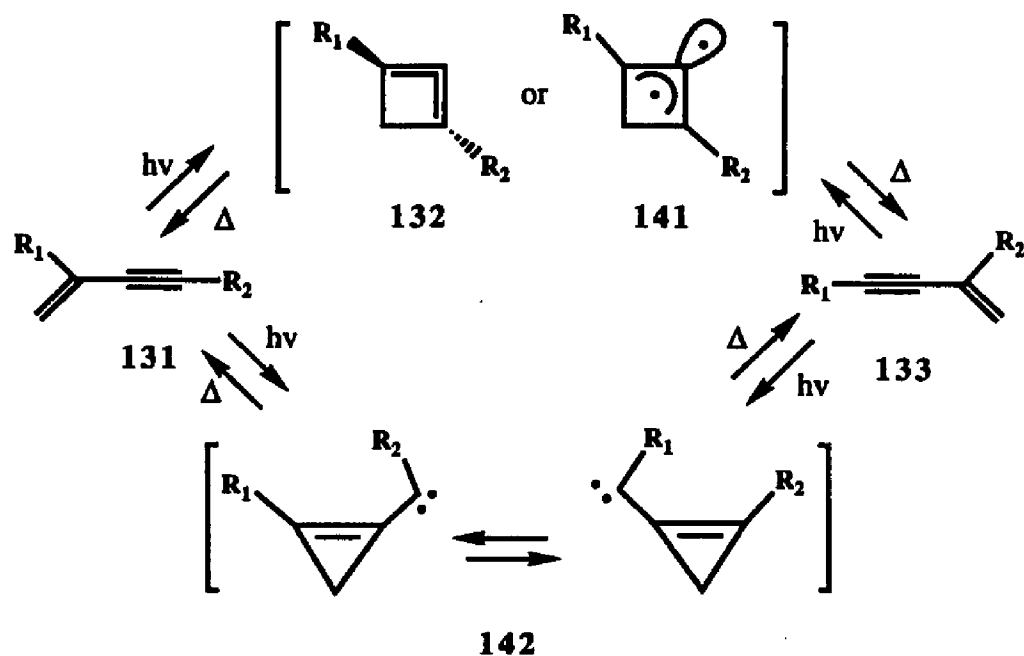
**Scheme 86**



Two potential mechanisms might explain the observed results. The intermediate formed during a concerted reaction may be pictured as 1,2-cyclobutadiene (**132**) or as a diradical structure (**141**). This rearrangement could also occur via a carbenic pathway, as shown in **Scheme 87**, in which carbene **142** is a possible intermediate.

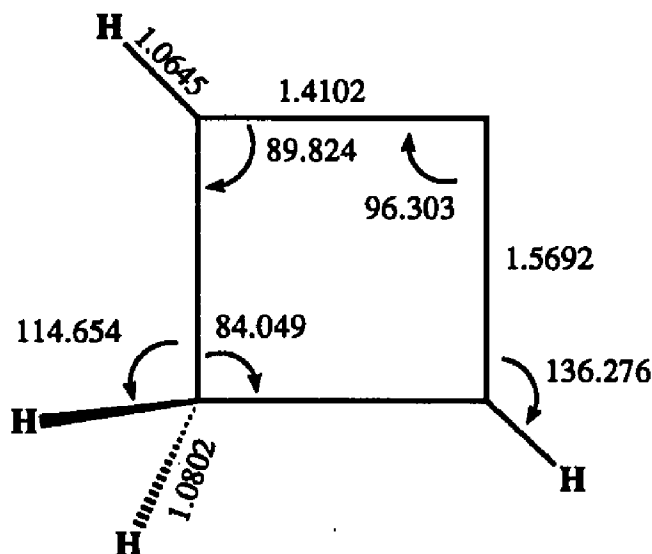
Ab initio molecular orbital calculations should provide some insight into the structure of 1,2-cyclobutadiene. In principle, this might be a chiral structure with C<sub>2</sub> symmetry (**132**), or a planar diradical (**141**). An important question is the energy of these

**Scheme 87**



species relative to vinylacetylene. Geometries for each of these species were optimized at various computational levels.<sup>129</sup> Vinylacetylene was optimized with an RHF/3-21G wavefunction. The structure for 1,2-cyclobutadiene was optimized with a singlet UHF/3-21G wavefunction, consistent with the open shell nature of this intermediate. The lowest state is of  $^1A_2$  symmetry, best described as the singlet diradical 141. Pertinent geometrical data are summarized in Figure 18. Frequency analysis showed this geometry to be a true energy minimum, since all positive frequencies were obtained. Subsequent calculations at the MP2/6-

**Figure 18.** Optimized geometrical parameters at the UHF/3-21G level for  $^1A_2$  1,2-cyclobutadiene (141). All bond lengths are in angstroms and all bond angles in degrees.



31G\* or MCSCF/3-21G levels confirm this analysis and indicate a modest barrier for ring opening .

A geometry for a chiral structure (132) was optimized with a TCSCF/STO-3G wavefunction. However, subsequent MCSCF calculations show this result to be an artifact of the wavefunction used.

The geometry for cyclopropenylcarbene 142 was also optimized with an RHF/3-21G wavefunction. In this case, a number of rotamers are possible; these are expected to have similar total

energies.

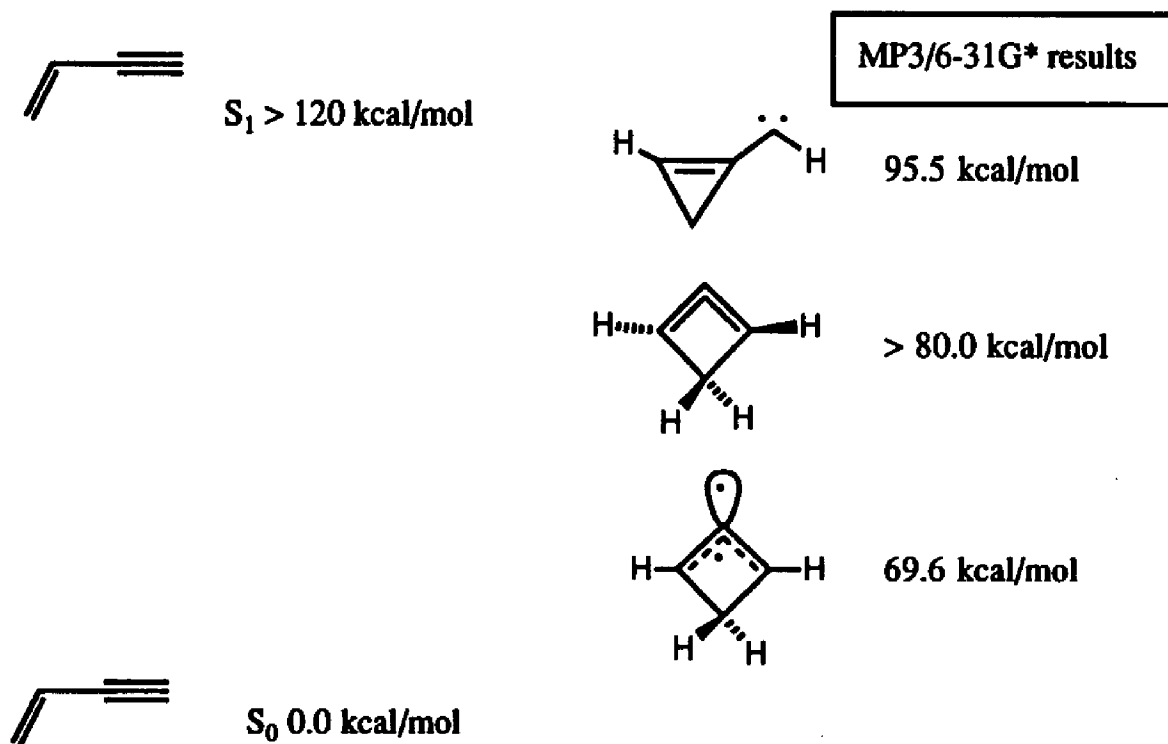
Final calculations at the MP3/6-31G\* level were carried out for all species; these results are summarized in Table 3.

**Table 3.** Results of Ab Initio Calculations (Energies in Hartrees)

<u>Species</u>	<u>Level of Calculation</u>		
	<u>HF/3-21G</u>	<u>HF/6-31G*</u>	<u>MP3/6-31G*</u>
vinylacetylene	-152.85621	-153.70779	-154.22442
141 ( <sup>1</sup> A <sub>2</sub> )	-152.77727	-153.64281	-154.11353
132 ( <sup>1</sup> A')	-152.72893 <sup>a</sup>	-153.57877	-154.09693
142	-152.69988	-153.56426	-154.07232

Figure 19 summarizes the relative energetics of the relevant species; the S<sub>1</sub> energy of vinylacetylene was obtained from UV spectroscopy.

Several important conclusions can be drawn from these calculations. First, it is apparent that 1,2-cyclobutadiene does correspond to an energy minimum, but this species is best described as a diradical rather than a closed shell allene. This completes the series of cyclic allenes. Second, the energy of 1,2-cyclobutadiene is predicted to be well below S<sub>1</sub> of vinylacetylene, which is permissive evidence that this species may be formed from the



**Figure 19.** Relative energetics for vinylacetylene, 1,2-cyclobutadiene, and cyclopropenylcarbene, calculated at the MP3/6-31G\* level.

singlet excited state. The chiral structure is not a true energy minimum; thus, the value given is only useful for comparison. Finally, cyclopropenylcarbene is significantly higher in energy, although still below the energy of the singlet excited state of vinylacetylene.

Further exploration of this portion of the  $C_4H_4$  potential surface is in progress.

## **EXPERIMENTAL SECTION**

### **General Experimental**

#### **Instrumentation**

**<sup>1</sup>H NMR Spectra** were recorded on a Bruker AM-360 Fourier transform spectrometer and a Varian EM-360A spectrometer. All spectra were measured with CDCl<sub>3</sub> as solvent and TMS as reference unless otherwise noted.

**<sup>13</sup>C NMR Spectra** were recorded at 90.52 MHz on a Bruker AM-360 Fourier transform spectrometer. All spectra were measured with CDCl<sub>3</sub> as solvent and TMS as reference unless otherwise noted.

**Infrared Spectra** were recorded on a Perkin-Elmer 283B grating spectrometer and a Nicolet 520 FT-IR spectrometer. Absorptions are reported in wavenumbers (cm<sup>-1</sup>), with polystyrene (1601 cm<sup>-1</sup>) as the calibration peak.

**Ultraviolet Spectra** were recorded on a Shimadzu Bausch & Lomb Spectronic 200 UV spectrometer.

**Low Resolution Mass Spectra** were obtained through the University Instrumentation Center on a Perkin-Elmer Hitachi RMU-60

mass spectrometer and a Hewlett-Packard 5988A spectrometer.

**Melting Points** were recorded on a MEL-TEMP capillary melting point apparatus, and are uncorrected.

**CHN Analyses** were obtained through the University Instrumentation Center on a Perkin-Elmer 240B elemental analyzer.

**Analytical Gas Chromatography** was performed with a Hewlett-Packard 5793A instrument equipped with a flame ionization detector and an attached model 3390A integrator. A crosslinked methyl silicone gum column (25m x 0.2 mm x 0.33  $\mu$ m) was employed.

**Preparative Gas Chromatography** was performed on a Varian 920 gas chromatograph with a glass-lined injector. The following columns were used: Apiezon, Carbowax, SE-30.

**High Pressure Liquid Chromatography** was performed on a Waters System, consisting of a series 440 absorbance detector and M-45 solvent delivery system. A  $\mu$ Porasil column was employed. A Hewlett-Packard model 3390A integrator was used for quantitative work.

### Photochemical Experiments

Spectroquality solvents were employed in all solution phase



photochemical experiments. Three different light sources were used: a Rayonet RPR-100 reactor, fitted with 254, 300, or 350 nm lamps, a 450 W Conrad-Hanovia lamp with sleeve filters, or a Bausch & Lomb 200 W mercury lamp with high intensity monochromator.

### Solvents

n-Pentane, n-hexane, and methylene chloride were distilled prior to use in column chromatography. Solvents distilled from calcium hydride and stored under nitrogen were dimethylsulfoxide (DMSO), diisopropylamine, cyclohexene, and cyclohexane. Tetrahydrofuran (THF) and diethyl ether (Et<sub>2</sub>O) were distilled under nitrogen immediately prior to use from purple sodium benzophenone ketyl. Ethylene glycol was distilled over magnesium sulfate.

### Column Chromatography and Adsorbents

Low temperature column chromatography (-20°C) was performed using a jacketed column, with temperature control maintained by a Lauda RC3 refrigerated recirculating bath.

Silica Gel used was 60-200 mesh, purchased from Davison Chemical. The silica gel was combined with Sylvania 2282 green

phosphor to permit UV observation when employing quartz columns.

**Alumina** was obtained from Baker or Aldrich. Mesh size of the neutral alumina was 50-200.

**Florisil** was purchased from Aldrich, mesh size 100-200.

**Flash Chromatography** silica gel was 200-425 mesh, and obtained from Fisher Scientific.

**Preparative TLC** utilized 1 mm silica gel plates, obtained from Analtech or Whatman. The plates were oven-dried prior to use.

## **Experimental**

### **Irradiation of Naphthalene and 1,2-Cyclononadiene**

Naphthalene (1.0 g, 8.0 mmol) and 1,2-cyclononadiene (2.0 g, 17 mmol) were dissolved in 200 mL of spectrophotometric-grade cyclohexane in a quartz vessel. The solution was degassed with a stream of nitrogen, and irradiated at 254 nm in a Rayonet apparatus for 89 hours. Progress was monitored by  $^1\text{H}$  NMR analysis of 10-mL aliquots, withdrawn at various intervals. The reaction was not carried to completion in order to avoid secondary photochemistry. The reaction mixture was concentrated on a rotary evaporator, and

eluted with hexane through a 3 x 56 cm silica gel column. The photoadducts were obtained in a combined 25% yield. The product consisted of three isomers, which were separated by preparative gas chromatography (Apiezon column, injector 230°C, column 250°C, detector 230°C). **Endo-14:**  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  0.27 (m, 1H),  $\delta$  0.86-1.64 (m, 9H),  $\delta$  2.07-2.14 (m, 2H),  $\delta$  2.37 (d, 1H,  $J = 4.9$  Hz),  $\delta$  3.79 (m, 1H),  $\delta$  4.27 (dd, 1H,  $J = 1.4, 7.4$  Hz),  $\delta$  5.37 (ddd, 1H,  $J = 1.8, 6.4, 8.2$ ),  $\delta$  6.45 (ddd, 1H,  $J = 1.4, 6.1, 7.4$ ),  $\delta$  6.65 (ddd, 1H,  $J = 1.6, 6.1, 7.6$ ),  $\delta$  7.07-7.21 (m, 4H). **Exo-13:**  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  1.18-1.43 (m, 8H),  $\delta$  1.88-2.06 (m, 4H),  $\delta$  2.25 (d, 1H,  $J = 9.6$  Hz),  $\delta$  3.87 (ddd, 1H,  $J = 2, 4.8$  Hz),  $\delta$  4.28 (dd, 1H,  $J = 1.6, 5.6$  Hz),  $\delta$  5.35 (ddd, 1H,  $J = 2.0, 6.5, 8.5$  Hz),  $\delta$  6.57 (ddd (2 overlapping), 2H,  $J = 1.7, 6.3, 7.6$  Hz),  $\delta$  7.04-7.20 (m, 4H). **Meta-15:**  $^1\text{H}$  NMR (partial, 360 MHz,  $\text{CDCl}_3$ )  $\delta$  2.96 (q, 1H,  $J = 2.8$  Hz),  $\delta$  3.28 (d, 1H,  $J = 5.3$  Hz),  $\delta$  5.37 (dd, 1H,  $J = 3.6, 7.0$ )

#### Irradiation of Naphthalene and 1,2-Nonadiene

1,2-Nonadiene (0.51 g, 4.0 mmol) and naphthalene (0.16 g, 1.3 mmol) were combined in a quartz test tube along with 60 mL

cyclohexane. The solution was degassed with nitrogen for 15 min and irradiated at 254 nm for 60 hours. Analysis by  $^1\text{H}$  NMR revealed resonances corresponding to 1,2-nonadiene and naphthalene. No photoproducts were in evidence.

#### Irradiation of Anthracene and 1,2-Cyclononadiene

Anthracene (1.0 g, 5.7 mmol), 1,2-cyclononadiene (2.1 g, 17 mmol), and 200 mL spectroscopic grade benzene were combined in a 200-mL pyrex photochemical vessel, equipped with magnetic stir bar, gas inlet, and cooling coils. Irradiation was conducted for 64 hours under argon. A fine, white precipitate was filtered from the reaction mixture, presumably anthracene dimer. The supernatant was concentrated, and analyzed by  $^1\text{H}$  NMR. No photoproducts were detected.

#### Synthesis of 7,7-Dichlorodibenzo [a:c] bicyclo [4.1.0] Heptane (22)

Phenanthrene (17.6 g, 0.099 mol) and cetyltrimethylammonium bromide (0.85 g, 2.3 mmol) were introduced into a 1000-ml, three-necked, round-bottomed flask, fitted with mechanical stirrer, condenser, and addition funnel. Chloroform (200 mL) was added, and

vigorous stirring begun. An aqueous sodium hydroxide solution (50%, 100 mL) was added dropwise through the addition funnel over 20 min, and the reaction mixture was stirred at room temperature for 3 days. The brown emulsion was poured into 1 L water in a 2-L separatory funnel, and extracted with 250 mL chloroform. The organic layer was carefully washed four times with 1 L water (note emulsion formation upon vigorous shaking). The chloroform layer was filtered through 300 g of basic alumina in a large sintered-glass funnel, which was then washed with an additional 300 mL of chloroform. Concentration of the filtrate produced a yellow-brown solid, which was recrystallized from ethanol. The resultant pale yellow solid (14.98 g, 58.00% yield) was collected, and subsequently recrystallized from hexane twice to give the long, white, fluffy needles characteristic of the product. Spectral data agreed with those reported in the literature (mp = 139-140°C, lit. mp = 141.5-142.5°C).<sup>46</sup>

#### Determination of Light Output by Ferrioxalate Actinometry

The actinometry solution was prepared by adding 2.9494 g potassium ferrioxalate to 600 mL distilled water in a 1000-mL

volumetric flask. Sulfuric acid (100 mL of a 1.0 N solution) was added to the flask, and the solution diluted to the mark with distilled water. The actinometry solution was stirred in the dark for one hour, and subsequently stored in the dark.

A 50-mL aliquot of actinometry solution was irradiated at 280 nm on the optical bench for 45.00 min (entrance slit, 5.4; exit slit, 3.0; photomultiplier counts, 300882). Aliquots of 2, 5, and 10 mL were transferred into 25-mL volumetric flasks. Phenanthroline solution (3 mL) and buffer solution (2 mL) were added to each flask. The solutions were diluted to the mark with distilled water, shaken, and stored in the dark for 30 min. The optical density for each solution was measured at 510 nm on a Bausch & Lomb Spectronic 70 Spectrophotometer. The concentration of  $\text{Fe}^{2+}$  was calculated from Equation 4, where  $\epsilon = 1.07 \times 10^4$  (determined experimentally by Equation 4

$$[\text{conc Fe}^{2+}] = \frac{\text{OD of complex at 510 nm}}{\epsilon \text{ (experimental) of Fe}^{2+} \text{ complex}}$$

calibrating absorbance vs. concentration for a standard  $\text{FeSO}_4$  solution). Light output (LOP) was determined from Equation 5. The ferrioxalate quantum yield,  $\phi = 1.24$  at 280 nm, was obtained

from the literature.<sup>47</sup>

### Equation 5

$$\text{LOP (mE/m)} = \frac{[\text{vol actinometer (mL)}] [\text{conc Fe}^{2+}] [\text{diluted vol (mL)}]}{[\phi \text{ Ferrioxalate}] [\text{vol aliquot (mL)}] [\text{time (min)}]}$$

### Determination of Quantum Yield for 22

Dichloro adduct **22** (0.031 g, 0.123 mmol) was placed in a quartz sample cell with 50 mL HPLC-grade hexane. The solution was degassed with a stream of nitrogen for 30 min, then irradiated on the optical bench at 280 nm for 2.00 hours. The solution was transferred to a 125-mL Erlenmeyer flask. A 5-mL aliquot of a standard naphthalene solution (1.068 mg/mL in hexane) was added to the flask as an internal standard. HPLC analysis of this solution provided the relative amounts of naphthalene, phenanthrene, and **22** present. Relative response factors for naphthalene and phenanthrene had previously been determined by analyzing standard solutions by HPLC. The amount of phenanthrene formed, 0.24 mg (0.00135 mmol), was calculated from this information.

LOP was determined prior to the irradiation by the method described above, and calibrated against photometer counts. The

amount of light absorbed by **22** during irradiation was 0.0177 mE.

**Equation 6** was used to calculate a quantum yield of 0.076 for this reaction.

**Equation 6**

$$\phi = \frac{\text{mmol product formed}}{\text{mE light absorbed}}$$

#### Photolysis of **22** and Benzophenone

Benzophenone (0.10 g, 0.55 mmol, recrystallized from ethanol), dichloro adduct **22** (0.052 g 0.20 mmol), and 50 mL of cyclohexane were combined in a large uranium glass tube and degassed with nitrogen. The solution was irradiated in the Rayonet using 350 nm lamps for 12 h. Progress of the reaction was monitored by TLC (silica plates, hexane). Formation of phenanthrene was not evident. <sup>1</sup>H NMR analysis of the mixture showed only reactants present.

#### Insertion of Dichlorocarbene Into Cyclohexane and 2-Methylpentane

A solution of **22** (0.011 g, 0.044 mmol) in 10 mL cyclohexane, fractionally distilled over CaH<sub>2</sub>, was placed in a quartz test tube, degassed under nitrogen, and irradiated in the Rayonet at 254 nm for



60 min. Progress of the reaction was followed using HPLC. Phenanthrene was generated during the course of the reaction, but no evidence for insertion products was noted.

Adduct 22 (0.055 g, 0.21 mmol) and 2-methylpentane (24.5 mL) were combined in a quartz test tube and degassed with nitrogen. The solution was irradiated at 254 nm in the Rayonet for 10 hours. Following concentration on a rotary evaporator,  $^1\text{H}$  NMR analysis revealed a singlet at  $\delta$  5.62, corresponding to dichlorocarbene insertion into the tertiary C-H bond. The sample was applied to a 1.5 x 28 cm silica gel column and eluted with pentane. The first fraction collected was injected into the analytical GC, however no peaks were detected.

#### Competition Study: Dichlorocarbene with Cyclohexene and Hexane

The dichloro adduct 22 was placed in four quartz test tubes, two containing cyclohexene and two containing hexane. Tube #1: 0.025 g (0.096 mmol) adduct and 25 mL hexane. Tube #2: 0.026 g (0.10 mmol) adduct and 25 mL hexane. Tube #3: 0.026 g (0.10 mmol) adduct and 25 mL cyclohexene. Tube #4: 0.026 g adduct (0.10 mmol) and 25 mL cyclohexene. The tubes were positioned in a merry-

go-round apparatus in the Rayonet and irradiated concurrently at 254 nm. The solutions were analyzed at 2, 10, and 20 min intervals by HPLC. The phenanthrene concentration was higher in the tubes containing hexane than in those with cyclohexene by an 8:1 ratio.

#### Irradiation of 22 and Naphthalene

Adduct 22 (0.021 g, 0.079 mmol) and naphthalene (0.024 g, 0.19 mmol) were combined in a Pyrex NMR tube with  $\text{CDCl}_3$  as solvent. A baseline  $^1\text{H}$  NMR of the sample was obtained. The NMR tube was irradiated on the optical bench with the 200 W lamp in the absence of the monochromator.  $^1\text{H}$  NMR spectra were recorded after 0.5, 1.0, and 3.0 h. Resonances corresponding to 22, naphthalene, and phenanthrene were recorded, however, no vinylic resonances arising from addition of dichlorocarbene to naphthalene were evident.

#### Synthesis of Benzyldichlorocarbene Precursor (30)

Adduct 22 (0.51 g, 1.9 mmol) and 15 mL freshly distilled THF were combined in a 50-mL, three-necked, round-bottomed flask, equipped with magnetic stir bar and nitrogen inlet. The flask was cooled to  $-78^\circ\text{C}$  in a dry ice/acetone bath, and 1.3 eq 2.5 M

n-butyllithium was added dropwise via syringe. The solution turned dark green, and was stirred at -78°C for 40 min. 2.0 mL (17 mmol) benzylbromide were added to the flask by syringe, and the resulting yellow solution held at -78°C for two hours. The reaction mixture was allowed to warm to room temperature, with stirring continued overnight. The solution was washed twice with 4 mL brine, dried over magnesium sulfate, filtered through glass wool, and concentrated on a rotary evaporator. TLC analysis of the yellow oil obtained (silica, 5% ether/hexane) gave three spots:  $R_f = 0.553$ , benzyl chloride;  $R_f = 0.319$ , benzylchloro adduct;  $R_f = 0.223$ , monochloro adduct. The product **30** was obtained as a white solid following column chromatography on florisil using 5% ether/hexane as eluent. mp 123.5-125.5°C;  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  2.93 (s, 2H),  $\delta$  3.39 (s, 2H),  $\delta$  7.27-7.41 (m, 11H),  $\delta$  8.02 (d, 2H,  $J = 7.5$ );  $^{13}\text{C}$  NMR  $\delta$  31.2, 43.0, 46.6, 122.7, 126.9, 127.2, 127.7, 128.4, 129.3, 130.3, 130.4, 131.8, 137.6; MS [ $m/z$ ] 316, 281 (M-Cl), 225 (M-C<sub>7</sub>H<sub>7</sub>). Anal. Calcd for C<sub>22</sub>H<sub>17</sub>Cl: C, 83.39; H, 5.42. Found: C, 83.79; H, 5.34.

### Photolysis of Benzychlorocarbene Precursor (30)

A solution of **30** (0.010 g, 0.033 mmol) in 13 mL optima-grade hexane was introduced into a quartz test tube and degassed with nitrogen. A baseline HPLC trace was obtained. The solution was irradiated in the Rayonet with 254 nm lamps. After 5 min, a 1  $\mu$ L sample was injected into the HPLC, showing three peaks with retention times of 2.86, 2.95, and 4.19 min. The first two peaks were presumed to be cis- and trans- $\beta$ -chlorostyrenes, while the peak at 4.19 is known from previous work to be phenanthrene. The same peaks were evident following an additional 5 min irradiation. The solution was concentrated;  $^1\text{H}$  NMR analysis of the crude product indicated resonances characteristic of the  $\beta$ -chlorostyrenes.  $^1\text{H}$  NMR (partial, crude material, 360 MHz,  $\text{CDCl}_3$ )  $\delta$  6.26 (d, 1H,  $J$  = 8.2 Hz)  $\delta$  6.63 (d, 1H,  $J$  = 8.5),  $\delta$  6.64 (d, 1H,  $J$  = 12.7),  $\delta$  6.84 (d, 1H,  $J$  = 13.7 Hz). The product mixture was applied to a preparative TLC plate (silica gel, 2% ether/hexane). No vinylic protons were evident in the bands collected, suggesting that the  $\beta$ -chlorostyrenes may have polymerized.

### Synthesis of Chloromethylcarbene Precursor (32)

Adduct **22** (0.507 g, 1.94 mmol) and 15 mL freshly distilled THF were combined in a 50-mL, three-necked, round-bottomed flask outfitted with magnetic stir bar and nitrogen inlet. The flask was immersed in a dry ice/acetone bath at  $-78^{\circ}\text{C}$ ; 1.0 mL (2.5 mmol) 2.5 M n-butyllithium was added dropwise via syringe, causing the solution to become dark green. After stirring at  $-78^{\circ}\text{C}$  for one-half hour, methyl iodide (1.0 mL, 16 mmol) was added to the flask by syringe. The yellow reaction mixture was stirred at  $-78^{\circ}\text{C}$  for two hours, then gradually warmed to room temperature. Stirring was continued overnight. The solution was washed twice with 4 mL of brine, dried over magnesium sulfate, and filtered through glass wool. Concentration afforded a yellow oil, which was purified by column chromatography (florisil, 2% ether/hexane). 0.25 g (53%) of a white solid were obtained. mp  $116\text{--}118^{\circ}\text{C}$ ;  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  1.86 (s, 1H),  $\delta$  2.65 (s, 1H),  $\delta$  7.14–7.34 (m, 6H),  $\delta$  7.98 (d, 2H,  $J = 7.7$  Hz).  $^{13}\text{C}$  NMR  $\delta$  24.7, 28.3, 32.3, 122.6, 127.1, 127.5, 130.2, 130.6, 131.5; IR (KBr pellet) 3008, 2960, 2926, 1487, 1447  $\text{cm}^{-1}$ ; MS [ $m/z$ ] 240, 205 (M-Cl). Anal. Calcd. for  $\text{C}_{16}\text{H}_{13}\text{Cl}$ : C, 79.82; H, 5.45. Found:

C, 80.09; H, 5.77.

#### Attempted Trapping of Chloromethylcarbene

Adduct **32** (0.011 g, 0.047 mmol) , 2 mL distilled cyclohexene, and 25 mL HPLC-grade pentane were combined in a quartz tube, and a baseline HPLC obtained. The solution was degassed under nitrogen, then irradiated at 254 nm. 1  $\mu$ L samples were injected into the HPLC after 15 and 30 min. of photolysis. The amount of adduct was observed to decrease during this time, while the amount of phenanthrene increased. The reaction mixture was concentrated and dissolved in CDCl<sub>3</sub> for NMR analysis. By <sup>1</sup>H NMR integration, phenanthrene was present in a 3:2 ratio over **32**. Numerous resonances were visible in the aliphatic region, however, the spectrum was too complex to permit assignment of the peaks to the trapped product.

#### Synthesis of Chlorocarbene Precursor (**31**)

Dichloro adduct **22** (0.517 g, 1.98 mmol) and 15 mL of freshly distilled THF were added to a 50-mL, three-necked, round-bottomed flask, outfitted with magnetic stir bar and nitrogen line. The flask

was cooled to  $-78^{\circ}\text{C}$  in a dry ice/acetone bath, whereupon n-butyllithium ( 0.8 mL of a 2.5 M solution, 2 mmol) was added dropwise via syringe, producing the green color characteristic of these reactions. After 0.5 h at  $-78^{\circ}\text{C}$ , 0.7 mL methanol was added to the flask by syringe, turning the solution yellow. The reaction mixture was stirred at  $-78^{\circ}\text{C}$  for 2 h, then gradually warmed to room temperature. After stirring overnight, the yellow solution was washed twice with 4 mL of brine, dried over magnesium sulfate, filtered, and concentrated. Both exo and endo isomers formed, as evidenced by two doublets at  $\delta$  2.7 and two triplets at  $\delta$  3.7 with coupling constants of 7.7 Hz. The  $^1\text{H}$  NMR spectrum of the endo chloro compound (31) matched that reported in the literature.<sup>64</sup>

#### Attempted Trapping of Chlorocarbene with Cyclohexene

Monochloro adduct 31 (0.010 g, 0.046 mmol), 2 mL cyclohexene, and 25 mL of pentane were combined in a quartz tube and degassed under nitrogen. The solution was irradiated at 254 nm in the Rayonet, and analyzed by HPLC at 0, 5, and 10 min. An increase in phenanthrene concentration was accompanied by a decrease in the amount of adduct present. TLC and  $^1\text{H}$  NMR indicated

no trapped products, only phenanthrene and starting material.

#### Carbenoid Quenching with Deuterated Methanol at -78°C

Dichloro adduct **22** (0.11 g, 0.42 mmol) and 4 mL distilled THF were introduced into a 25-mL, three-necked, round-bottomed flask, equipped with nitrogen inlet and magnetic stir bar. The flask was cooled to -78°C using a dry ice/acetone bath, and n-butyllithium (0.2 mL of a 2.5 M solution, 0.5 mmol) added dropwise via syringe. The deep green solution was stirred at -78°C for 45 min, at which point CD<sub>3</sub>OD (1.0 g, 28 mmol) was added, turning the solution pale yellow. The reaction mixture was warmed to room temperature, then worked up in the flask with the addition of 4 mL brine. The bottom layer was pipetted off, and the organic layer dried with magnesium sulfate. Filtration through a plug of glass wool, followed by concentration, produced a white solid, which was applied to a prep TLC plate (2% ether/hexane). A broad band was visualized about a third of the way up the plate; the top half of this band was collected as one fraction, and the bottom half of the band, along with a small, narrow band just below it, was collected as a second fraction. <sup>1</sup>H NMR analysis of the leading edge implied formation of a



phenanthrene derivative. The  $^1\text{H}$  NMR spectrum of the trailing edge was consistent with formation of the chlorodeutero adduct.  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  2.97 (s, 2H),  $\delta$  7.29-7.42 (m, 8H),  $\delta$  8.04 (d, 2H,  $J = 7.6$ ).  $^{13}\text{C}$  NMR  $\delta$  24.7, 122.6, 127.2, 127.7, 129.2, 130.4, 132.2. MS [m/z] 227.

#### Carbenoid Quenching with Deuterated Methanol at 0°C

Adduct 22 (0.10 g, 0.37 mmol) and 4 mL distilled THF were combined in a 25-mL, three-necked, round-bottomed flask, outfitted with a magnetic stir bar and nitrogen line. Stirring was begun, and the flask immersed in a dry ice/acetone bath at  $-78^\circ\text{C}$ . n-Butyllithium (0.2 mL of a 2.5 M solution, 0.5 mmol) was added dropwise via syringe, turning the solution a deep green. The reaction mixture was allowed to warm to  $0^\circ\text{C}$ , then  $\text{CD}_3\text{OD}$  (1.0 g, 28 mmol) was added, changing the color to a vibrant yellow after several drops. Work-up was done in the flask by adding 4 mL of brine and removing the aqueous layer with a Pasteur pipette. The reaction mixture was dried over magnesium sulfate, filtered through glass wool, and concentrated, leaving an orange oil. Two bands were collected following application of the oil to a prep TLC plate (silica

gel, 2% ether/hexane). Analysis of the leading band by  $^1\text{H}$  NMR strongly suggested formation of 9-n-pentylphenanthrene.  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  .90 (t, 3H,  $J = 7.2$ ),  $\delta$  1.33-1.55 (m, 6H),  $\delta$  2.28 (d, 2H,  $J = 3.9$ ),  $\delta$  7.22-7.24 (m, 3H),  $\delta$  7.38-7.40 (m, 2H),  $\delta$  7.58-7.7 (m, 2H),  $\delta$  7.89-7.96 (m, 3H),  $\delta$  8.70 (d, 1H,  $J = 8.0$  Hz). MS [ $m/z$ ] 248.

#### Synthesis of 7,7-Dibromodibenzo [a:c] bicyclo [4.1.0] heptane (36)

Potassium *t*-butoxide (22.76 g, 0.2028 mol) and phenanthrene (30.56 g, 0.1717 mol) were added to 260 mL distilled ether in a 1000-mL, three-necked, round-bottomed flask, equipped with nitrogen line, addition funnel, and mechanical stirrer. Stirring was begun, and the flask immersed in an ice bath. Bromoform (15 mL, 0.17 mol) was added dropwise over 20 min. The reaction mixture was stirred at  $0^\circ\text{C}$  for one hour, followed by one-half hour at room temperature. 400 mL water were added to the flask with stirring. The solution was transferred to a 1000-mL separatory funnel, where the aqueous layer was extracted with methylene chloride (3 x 50 mL). The combined organic extracts were dried over magnesium sulfate, filtered, and concentrated to a volume of about 200 mL. A yellow solid precipitated from the reaction mixture upon standing

over the weekend. The product was collected on a sintered glass funnel, and recrystallized from a 2 : 1 mixture of pentane : methylene chloride. The product (**36**) was obtained as a white solid in 10% yield (6.2 g). Spectral data agreed with that reported in the literature.<sup>59</sup>

#### Attempted Trapping of Dibromocarbene

Adduct **36** (0.011 g, 0.030 mmol), 2 mL distilled cyclohexene, and 25 mL distilled pentane were combined in a quartz test tube. The reaction mixture was irradiated in the Rayonet at 300 nm. HPLC analysis was performed on the sample at 0, 2, 4, and 9 min, showing an increase in the amount of phenanthrene present. Concentration of the sample, followed by <sup>1</sup>NMR analysis, revealed a multitude of peaks, none of which could be assigned to the trapped carbene. Numerous photoproducts are evident in the <sup>1</sup>H NMR spectrum even after one minute irradiation. A dark experiment proved that the products formed are the result of irradiation.

#### Reaction of **22** with n-Butyllithium and Cyclooctene

Dichloro adduct **22** (0.11 g, 0.39 mmol) and 4 mL distilled THF

were introduced into a 25-mL, three-necked, round-bottomed flask, equipped with magnetic stir bar and nitrogen line. The flask was immersed in a dry ice/acetone bath at  $-78^{\circ}\text{C}$ , and n-butyllithium (0.2 mL of a 2.5 M solution, 0.5 mmol) added via syringe. The green solution was stirred at  $-78^{\circ}\text{C}$  for 45 min, whereupon distilled cyclooctene (0.20 mL, 1.5 mmol) was added. The reaction mixture was warmed to room temperature. A canary-yellow precipitate formed in the reaction flask upon warming. The solid dissipated with the addition of 4 mL of brine. The aqueous layer was removed by Pasteur pipette, and the organic layer dried over magnesium sulfate. Following filtration and concentration, the  $^1\text{H}$  NMR indicated formation of the monochloro adduct. No upfield resonances, indicative of a spiropentane product, were present.

Two variations on this protocol were implemented. In the first case, the reaction mixture was stirred at room temperature for 10 h prior to work-up. The second effort required heating the reaction mixture at  $50^{\circ}\text{C}$  for 12 h after reaching room temperature. Both cases saw formation of the monochloro adduct.

#### Reaction of 36 with n-Butyllithium and Cyclooctene

Adduct **36** (0.010 g, 0.029 mmol) and 2 mL THF were combined in a 25-mL, three-necked, round-bottomed flask, outfitted with magnetic stir bar and nitrogen line. n-Butyllithium (0.05 mL of a 2.5 M solution, 0.1 mmol) was added via syringe to the flask, which had been cooled to -78°C in a dry ice/acetone bath. The yellow solution was stirred for 30 min at -78°C. Cyclooctene (0.03 mL, 0.2 mmol) was added dropwise, and the reaction mixture gradually warmed to room temperature. After 10 h stirring, work-up was performed in the flask with the addition of 2 2-mL portions brine. The aqueous layer was removed, and the organic layer dried over magnesium sulfate, then concentrated to yield 5.7 mg (13%) of a yellow oil. The oil was dissolved in ether and applied to a preparative TLC plate (5% ether/hexane). An intense band was collected, eluted, and concentrated, yielding a white solid. The product was identified as the fully reduced product **37**, confirmed by comparison with the published <sup>1</sup>H NMR spectrum.<sup>64</sup>

#### Reaction of 36 with n-Butyllithium and Cyclohexene

Dibromo adduct **36** (0.514 g, 1.47 mmol) and 15 mL distilled THF

were introduced into a 25-mL, three-necked, round-bottomed flask, fitted with magnetic stir bar and nitrogen line. Cyclohexene (0.50 mL, 4.9 mmol), distilled from calcium hydride, was added, and the flask cooled to -78°C in a dry ice/acetone bath. n-Butyllithium (0.60 mL of a 2.5 M solution, 1.5 mmol) was added dropwise via syringe. The yellow solution was stirred at -78°C for three h, and gradually warmed to room temperature. The reaction mixture was washed with brine (2 x 4 mL), filtered, and concentrated. The <sup>1</sup>H NMR spectrum of this sample showed the major product to be the monobromo adduct, accompanied by formation of the fully reduced product.

#### Synthesis of 8,8-Dibromo-1-Methoxybicyclo [5.1.0] Octane (79)

Potassium *t*-butoxide (5.94 g, 52.9 mmol) and 50 mL pentane were combined in a 250-mL, three-necked, round-bottomed flask, equipped with nitrogen inlet, mechanical stirrer, and addition funnel. The flask was immersed in an ice bath and stirring begun. 1-Methoxycycloheptene (5.14 g, 40.8 mmol) was added, turning the solution a brilliant yellow. Bromoform (4.2 mL, 48 mmol) was added dropwise through the addition funnel, causing the reaction

mixture to become orange, then brown. Stirring was continued overnight at room temperature. After 21 h, the flask was again cooled to 0°C and carefully quenched with water. The mixture was transferred to a 500-mL separatory funnel, where the aqueous layer was extracted with pentane (3 x 50 mL). The combined organic extracts were washed with water (3 x 50 mL), dried over sodium sulfate, filtered, and concentrated. 12.0252 g of an orange oil were realized. Residual bromoform was removed by heating the oil to 40°C under reduced pressure. Purification of the product was accomplished by eluting the oil with hexane through 100 g alumina. The fractions were concentrated and placed in the freezer to induce crystallization. 4.7 g (39%) of an off-white solid, mp 37°C, were obtained. <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>) δ 1.13-1.21 (m, 2H), δ 1.39-1.87 (m, 7H), δ 2.24-2.28 (m, 1H), δ 2.43-2.49 (m, 1H), δ 3.45 (s, 3H); <sup>13</sup>C δ 25.0, 27.2, 27.4, 29.5, 31.5, 42.1, 45.4, 54.1, 70.4; IR (neat) 3010, 2960, 2940, 2850, 2820, 1450, 1225, 1120, 1075, 1045 cm<sup>-1</sup>; MS [m/z] 295 (M-1). Anal. Calcd. for C<sub>9</sub>H<sub>14</sub>OBr<sub>2</sub>: C, 36.27%; H, 4.74%. Found: C, 35.89%; H, 4.73%.

### Synthesis of 2-(Trimethylsilyl)-2-Cyclooctenone (76)

Dibromo compound **79** (3.0 g, 10 mmol) and 20 mL dry THF were combined in a 50-mL, three-necked, round-bottomed flask, outfitted with magnetic stir bar and nitrogen line. The flask was cooled to -78°C in a dry ice/acetone bath. n-Butyllithium (4.8 mL of a 2.5 M solution, 12 mmol) was added dropwise by syringe, and the reaction mixture stirred for 30 min at -78°C. Chlorotrimethylsilane ( 3.8 mL, 30 mmol) was added via syringe. The solution was held at -78°C for two h, then allowed to warm to room temperature. The reaction mixture was slowly quenched with water, then transferred to a 250-mL separatory funnel. The aqueous layer was extracted three times with 25-mL portions ether. The combined ethereal extracts were washed twice with 25 mL water, dried over sodium sulfate, filtered, and concentrated to give 8.1465 g of a pale yellow oil.

The oil was combined with 20 mL methanol and potassium carbonate (4.0 g, 29 mmol) in a 50-mL, round-bottomed flask. The reaction mixture was refluxed overnight under nitrogen. After cooling, water was added to the flask, and the solution transferred to a 250-mL separatory funnel. The aqueous layer was extracted



with ether (3 x 25 mL). The combined organic extracts were washed with water (2 x 25 mL), dried over magnesium sulfate, filtered and concentrated. 4.3961 g of a yellow oil were obtained.

This oil was stirred for one hour under nitrogen with 10 mL THF and 10 mL 5% sulfuric acid. Following the addition of water, the reaction mixture was transferred to a 250-mL separatory funnel. The aqueous layer was extracted twice with 25 mL ether. The ethereal extracts were combined and washed twice with 25 mL water, dried over magnesium sulfate, filtered, and concentrated. 3.5992 g of a yellow oil were obtained, which was purified by column chromatography (silica gel, 2% ether/hexane). The product was obtained as a clear oil in 27.26% yield (0.5343 g).  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  0.11 (s, 9H),  $\delta$  1.62 (m, 4H),  $\delta$  1.87 (m, 2H),  $\delta$  2.29 (m, 2H),  $\delta$  2.36 (m, 2H),  $\delta$  6.17 (t, 1H,  $J = 4.3$ );  $^{13}\text{C}$  NMR  $\delta$  -1.6, 21.7, 21.9, 29.6, 33.1, 45.1, 142.9, 143.3, 215.8; IR (neat): 3005, 2950, 2920, 2885, 1670, 1610, 1255, 1010, 840  $\text{cm}^{-1}$ ; MS [ $m/z$ ] 197 ( $M+1$ ). Anal. Calcd. for  $\text{C}_{11}\text{H}_{20}\text{OSi}$ : C, 67.28; H, 10.27%. Found: C, 66.95%; H, 10.42%.

Synthesis of 2-Trifluoromethanesulfonic-3-trimethylsilyl-1,3-cyclooctadiene (82)

Lithium diisopropylamide (LDA) was generated *in situ* by combining diisopropylamine (0.15 mL, 1.1 mmol) , in 5 mL THF at -78°C, with n-butyllithium (0.45 mL of a 2.5 M solution, 1.1 mmol). Enone 76 (0.204 g, 1.04 mmol) was dissolved in 1 mL THF and added dropwise to the reaction flask via syringe. The yellow solution was held at -78°C for two h, at which point N-phenyltriflimide (0.39 g, 1.1 mmol) was added as a solid. The flask was gradually warmed to 0°C, and the dry ice/acetone bath replaced with an ice bath. The reaction mixture was stirred overnight under nitrogen. The orange solution was poured into 100 mL water in a 250-mL separatory funnel, and extracted with pentane. The aqueous layer was extracted with pentane (2 x 50 mL). The combined organic extracts were washed with water (2 x 50 mL), dried over magnesium sulfate, filtered, and concentrated. Cold hexane was added to the flask to precipitate out some of the excess triflimide. The presence of two triplets at  $\delta$  5.72 and  $\delta$  6.33 in the  $^1\text{H}$  NMR suggested formation of the expected diene. Purification of the product on a 3 x 83 cm silica gel column led to decomposition of the product. Purification on

florisil was also unsuccessful, leading to rearrangement. Microdistillation of the product resulted in decomposition as well.

#### Reaction of 82 with Cesium Fluoride

Diphenylisobenzofuran (0.045 g, 0.17 mmol) , cesium fluoride (0.072 g, 0.48 mmol), and 2 mL dry DMSO were combined in a 10-mL, round-bottomed flask, fitted with stir bar and nitrogen line. Triflate 82 ( 0.057 g, 0.17 mmol) was dissolved in 0.2 mL DMSO, then added to the flask by syringe. The orange solution was stirred overnight at room temperature. The reaction mixture was poured into 10 mL water in a 250-mL separatory funnel and extracted with ether. The aqueous layer was extracted with ether (3 x 10 mL). The combined ethereal extracts were washed with water (2 x 10 mL), dried over magnesium sulfate, filtered, and concentrated, affording 0.0806 g of a yellow film. The film was redissolved in ether and applied to a preparative TLC plate (silica gel, 3 : 2 hexane : ether). Three bands were collected, with  $R_f$  values of 0.67, 0.50, and 0.14. The leading band displayed a triplet at  $\delta$  5.64, indicative of the trapped product. Since two other triplets, at  $\delta$  4.61 and  $\delta$  6.09, were present in the spectrum, the sample was applied to a second preparative TLC plate

(silica gel, 3 : 1 hexane : dichloromethane). Collection of the trailing band from this plate again yielded the same three triplets. Mass spectrum of this sample gave a molecular ion peak of 376, in accord with the molecular weight of the trapped butatriene.

#### Synthesis of 2-Chloro-3-Trimethylsilyl-1,3-Cyclooctadiene (86)

Enone **76** (0.12 g, 0.60 mmol) and  $\text{PCl}_5$  (0.14 g, 0.65 mmol) were introduced into a 10-mL, round-bottomed flask, under nitrogen. The flask was cooled to 0°C in an ice bath, whereupon phosphorous oxychloride (0.06 mL, 0.64 mmol) was added by syringe. The brown solution was stirred for 20 h at room temperature. The flask was recooled to 0°C, and the reaction mixture added dropwise (caution!) to a saturated sodium bicarbonate solution. The mixture was transferred to a 125-mL separatory funnel and extracted with ether. The aqueous layer was extracted twice with 25 mL ether. The combined organic extracts were washed twice with 25 mL water, dried over magnesium sulfate, filtered, and concentrated. Purification was achieved by elution with pentane through a short alumina column. The product was collected as a clear oil (0.029 g, 22% yield).  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  0.15 (s, 9H),  $\delta$  1.55-1.75 (m,

4H),  $\delta$  2.05-2.33 (m, 4H),  $\delta$  5.79 (t, 1H,  $J = 8.4$  Hz),  $\delta$  6.11 (dd, 1H,  $J = 1.4, 7.2$ );  $^{13}\text{C}$   $\delta$  -0.9, 22.8, 23.7, 27.9, 29.1, 126.7, 133.4, 138.6, 143.7.

#### Reaction of 86 with Cesium Fluoride

Diene **86** (0.030 g, 0.14 mmol), diphenylisobenzofuran (0.038 g, 0.14 mmol), and 2 mL DMSO were combined in a 10-mL, round-bottomed flask under nitrogen. Cesium fluoride (0.066 g, 0.44 mmol) was added as a solid, and the yellow solution stirred for 37 h at ambient temperature, followed by 12 h at 40°C. After cooling, the mixture was poured into 10 mL water in a 125-mL separatory funnel and extracted with ether. The aqueous layer was extracted with ether (3 x 10 mL). The organic extracts were combined, washed with water (2 x 10 mL), dried over magnesium sulfate, filtered, and concentrated. The product was dissolved in methylene chloride and applied to a preparative TLC plate (silica gel, 5% ether/hexane). The product was contained in a band with  $R_f = 0.639$ . 3.3 mg of a pale yellow solid were collected (7.3% yield).  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  1.60-1.63 (m, 4H),  $\delta$  2.16-2.22 (m, 2H),  $\delta$  2.27-2.31 (m, 2H),  $\delta$  5.65

(t, 2H, J = 6.5 Hz),  $\delta$  7.17 (dd, 2H, J = 3.0, 5.4 Hz),  $\delta$  7.38 (dd, 2H, J = 3.0, 5.4 Hz),  $\delta$  7.43 (tt, 2H, J = 7.3 Hz),  $\delta$  7.51 (tt, 4H, J = 7.2 Hz),  $\delta$  7.81-7.84 (dt, 4H, J = 1.4, 7.1 Hz);  $^{13}\text{C}$   $\delta$  24.7, 27.2, 119.4, 123.8, 126.5, 127.6, 128.0, 128.4, 135.8, 141.8, 147.3; MS [m/z] 376; UV (95% EtOH)  $\lambda_{\text{max}}$  257 ( $\epsilon$  4558), 209 ( $\epsilon$  22,934).

**Control Experiment: Reaction of 86 with Diphenylisobenzofuran**

Diene **86** (0.011 g, 0.079 mmol) , diphenylisobenzofuran (0.23 g, 0.087 mmol), and 0.5 mL distilled DMSO were combined in a 10-mL, round-bottomed flask. The reagents were stirred under nitrogen at 45°C for 15 h. After cooling, the reaction mixture was poured into 10 mL water in a separatory funnel and extracted with ether. The aqueous layer was extracted three times with 10-mL portions ether. The ethereal extracts were combined, washed three times with 10 mL water, dried over magnesium sulfate, filtered, and concentrated.  $^1\text{H}$  NMR analysis showed the starting diene to be unchanged. A portion of diphenylisobenzofuran had reacted with singlet oxygen to form 1,2-dibenzoylbenzene, confirmed by comparison with the Aldrich spectrum.

#### **NMR Experiment: Attempt to Directly Observe 1,2,3-Cyclooctatriene**

Diene **86** (5.1 mg, 0.024 mmol) was dissolved in an NMR tube with DMSO- $d_6$ , and a baseline NMR spectrum recorded. Cesium fluoride (12.3 mg, 0.0810 mmol) was added, and the tube purged with nitrogen. After 48 h at room temperature, no change in the  $^1\text{H}$  NMR spectrum was noted. The tube was heated at 45°C for 37 h under nitrogen. The vinylic triplets arising from the starting material had diminished in size, and new olefinic resonances were evident. These resonances could not, however, be assigned to 1,2,3-cyclooctatriene.

#### **Synthesis of 1-Trimethylsilyl-5-Chloro-Cyclopentene (112)**

Alcohol **111** (0.057 g, 0.37 mmol) and 2 mL spec grade  $\text{CCl}_4$  were combined in a 10-mL, round-bottomed flask, and purged with nitrogen. The flask was cooled to 0°C in an ice bath, and thionyl chloride (0.05 mL, 0.7 mmol) added dropwise via syringe. The ice bath was removed after 15 min stirring. The solution was stirred for an additional 1h and 45 min at ambient temperature. TLC of the reaction mixture (silica, 10% ether/hexane) gave one spot,  $R_f = 0.694$ . Concentration of the sample produced 0.046 g (73% yield) of a brown oil.  $^1\text{H}$  NMR (360 MHz,  $\text{CDCl}_3$ )  $\delta$  0.15 (s, 9H),  $\delta$  2.16-2.41 (m,

3H),  $\delta$  2.58-2.69 (m, 1H),  $\delta$  5.10 (ddd, 1H,  $J = 1.8, 3.5, 6.7$  Hz),  $\delta$  6.23 (t,  $J = 2.3$  Hz);  $^{13}\text{C}$   $\delta$  -1.1, 33.0, 36.2, 69.6, 142.6, 145.9.

### Synthesis of 1-Phenylcyclobutene

1-Phenylcyclobutanol (0.90 g, 6.1 mmol) and 8 mL pyridine were placed in a 25-mL, three-necked, round-bottomed flask, outfitted with stir bar and nitrogen line. The flask was cooled to 0°C, whereupon phosphorous tribromide (0.7 mL, 7 mmol) was added dropwise via syringe. The yellow slurry was stirred at 0°C for 1.5 h, then poured onto ice water. The mixture was transferred to a 250-mL separatory funnel and extracted with cold ether. The aqueous layer was extracted with cold ether (3 x 25 mL). The ether extracts were combined and washed with cold water (2 x 25 mL), dried over magnesium sulfate, filtered, and concentrated cold. The crude product mixture was purified by column chromatography (3 x 43 cm, silica gel, pentane). 0.1011 g (12.83% yield) of a pale yellow oil were obtained. Spectral data agreed with those in the literature.

### Addition of Dichlorocarbene to 1-Phenylcyclobutene

Alkene 117 (0.18 g, 1.4 mmol), benzyltriethylammonium



chloride (0.1 g, 0.4 mmol), and 10 mL chloroform were introduced into a 250-mL, three-necked, round-bottomed flask. Mechanical stirring was begun and the flask cooled to 0°C in an ice bath. Sodium hydroxide (1 mL of a 50 M solution) was added, turning the clear solution brown. Stirring under nitrogen at 0°C was continued for five h. The reaction mixture was quenched with ice water, then transferred to a 250-mL separatory funnel. The aqueous layer was extracted three times with cold ether. The combined organic extracts were washed twice with cold water and dried over magnesium sulfate. A portion of the yellow ethereal solution was concentrated cold for NMR analysis. The <sup>1</sup>H NMR spectrum was quite complex; however, the presence of a resonance at δ 5.05 (dt, J = 2.0, 7.3 Hz) indicated formation of the rearranged product, rather than the cycloadduct. After sitting at room temperature for 24 h, no change in the spectrum was observed.

#### Attempted Synthesis of 1-Phenyl-1,2-Cyclopentadiene

The product from the previous reaction (0.101 g, 0.478 mmol), diphenylisobenzofuran (0.130 g, 0.482 mmol), and 6 mL distilled ether were introduced into a 10-mL, round-bottomed flask under

nitrogen. The flask was cooled to 0°C in an ice bath, and methyllithium (0.4 mL of a 1.4 M solution, 0.6 mmol) added dropwise via syringe. The yellow-brown solution was stirred for one hour at 0°C. The reaction mixture was carefully quenched with water, then transferred to a 250-mL separatory funnel. The aqueous layer was extracted with ether (2 x 10 mL). The combined organic extracts were washed with water (2 x 10 mL), dried over magnesium sulfate, filtered, and concentrated. The <sup>1</sup>H NMR spectrum was nearly identical with starting material. No resonances assignable to trapped product were evident.

#### Photochemical Addition of Dichlorocarbene to 1-Phenylcyclobutene

1-Phenylcyclobutene (0.0209 g, 0.161 mmol) and **22** (0.081 g, 0.31 mmol) were combined in an NMR tube with CDCl<sub>3</sub>. The tube was placed in a Dewar flask filled with ice water and irradiated on the optical bench without the monochromator for one hour. <sup>1</sup>H NMR revealed phenanthrene formation, as well as the disappearance of the vinylic resonance in the starting alkene. Again, no resonances indicative of carbene addition were evident.

### Addition of Dibromocarbene to 1-*t*-Butylcyclohexene

1-*t*-Butylcyclohexene (0.107 g, 0.775 mmol) , potassium *t*-butoxide (0.185 g, 1.64 mmol), and 6 mL pentane were combined in a 50-mL, three-necked, round-bottomed flask, equipped with stir bar and nitrogen line. An ice bath was placed around the flask, and bromoform ( 0.13 mL, 1.5 mmol) added dropwise via syringe to the bright yellow suspension. The reaction mixture was gradually warmed to room temperature, then stirred for 26 h under nitrogen. Water was slowly added to the flask, and the solution transferred to a 250-mL separatory funnel. The aqueous layer was extracted twice with 25-mL portions ether. The combined ether extracts were washed twice with 25-mL portions water, dried over magnesium sulfate, filtered, and concentrated, yielding 0.3589 g of a yellow oil. Two resonances in the  $^1\text{H}$  NMR at  $\delta$  5.48 and  $\delta$  5.67 implied insertion of the carbene into a C-H bond. The  $^{13}\text{C}$  spectrum clearly showed formation of both addition and insertion products: addition (partial)  $\delta$  18.6, 19.6, 21.9, 23.8, 28.0, 78.1; insertion  $\delta$  24.5, 25.2, 26.9, 28.2, 28.9, 36.2, 46.8, 115.9, 150.4. Purification was attempted by low temperature column chromatography on florisil (-20°C, 1.5 x 24 cm, hexane) . The cycloadduct was not isolated as a pure compound,

however.

#### Addition of Dichlorocarbene to 1-*t*-Butylcyclohexene

1-*t*-Butylcyclohexene (0.134 g, 0.973 mmol), cetyltrimethylammonium bromide (0.0534 g, 0.147 mmol), and 3 mL chloroform were combined in a 100-mL, three-necked, round-bottomed flask, fitted with condenser, addition funnel, and magnetic stir bar. The reaction mixture was heated to 56°C. Sodium hydroxide solution (5 mL, 12.7 M) was added dropwise through the addition funnel. The solution was held at 56°C for 2 h; an additional 6 mL CHCl<sub>3</sub> was added, as the mixture became quite viscous. Stirring was continued overnight. The reaction mixture was quenched with water and transferred to a 250-mL separatory funnel. The aqueous layer was extracted with ether (2 x 50 mL), the combined organic layers washed with water (2 x 50 mL), dried over magnesium sulfate, filtered, and concentrated. 0.205 g (95.7 %) of a clear oil were realized. The NMR spectrum recorded for the product mixture was virtually identical to that obtained upon addition of dibromocarbene to 1-*t*-butylcyclohexene.

### **Photochemical Addition of Dichlorocarbene to 1-*t*-Butylcyclohexene**

1-*t*-Butylcyclohexene (0.0725 g, (0.525 mmol) and **22** (0.283 g, 1.08 mmol) were combined with 2 mL dichloromethane and 3 mL hexane in a small quartz test tube. The solution was degassed with nitrogen and irradiated at 254 nm in the Rayonet for 3 h. Progress of the reaction was monitored by TLC. Phenanthrene formation was evident by  $^1\text{H}$  NMR, but no product arising from addition of dichlorocarbene to the alkene was detected.

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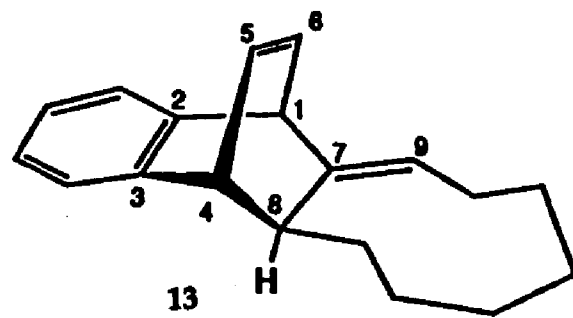
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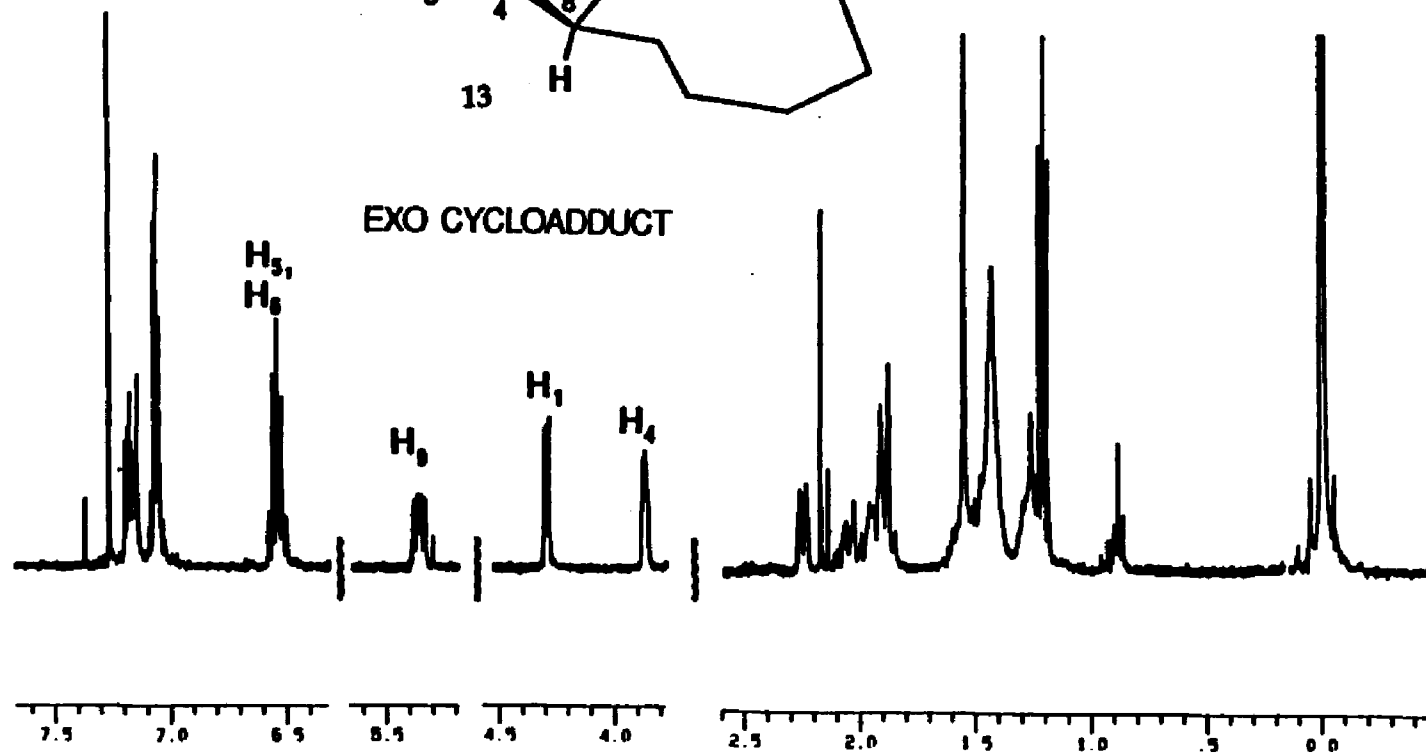
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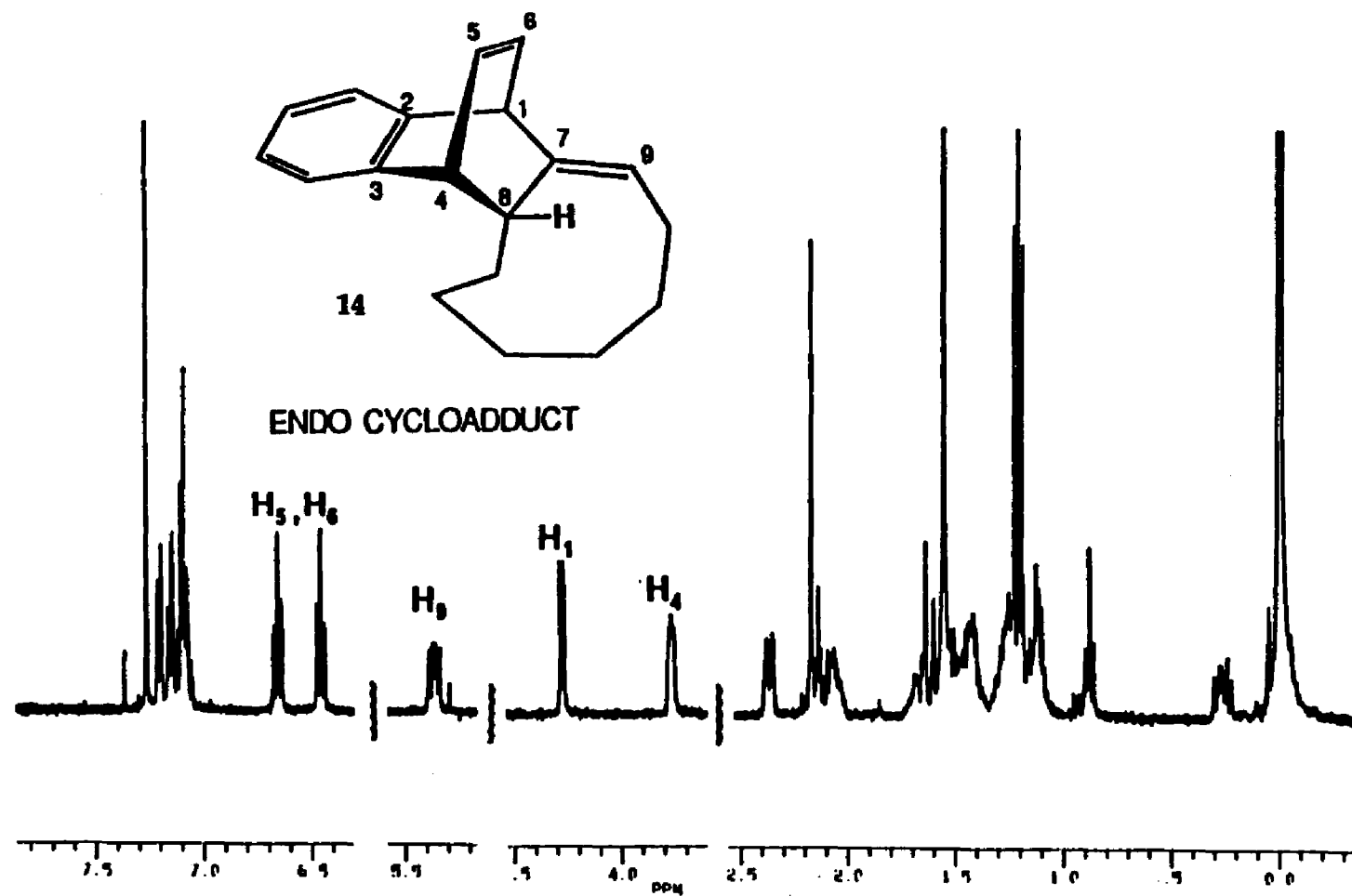
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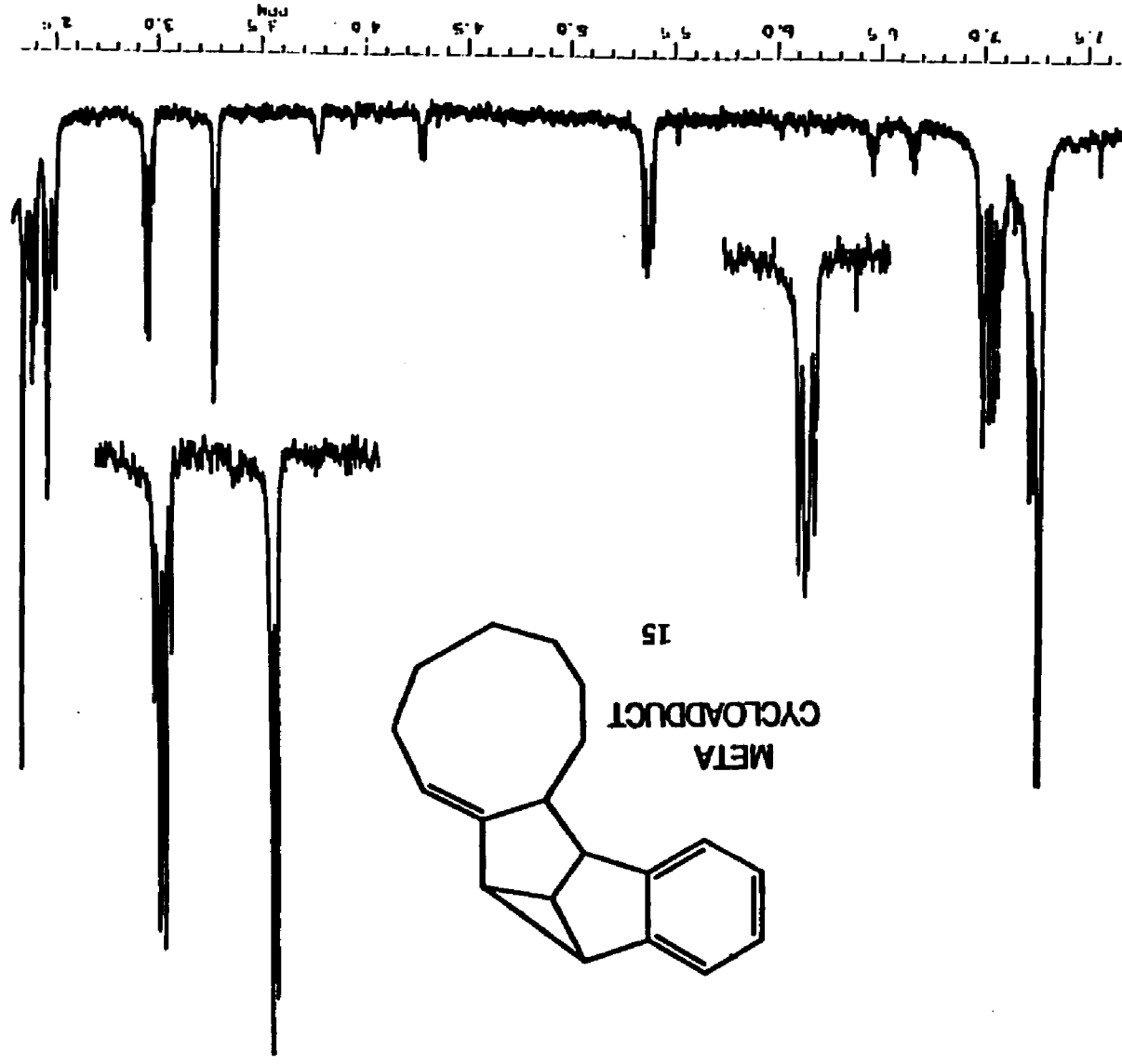


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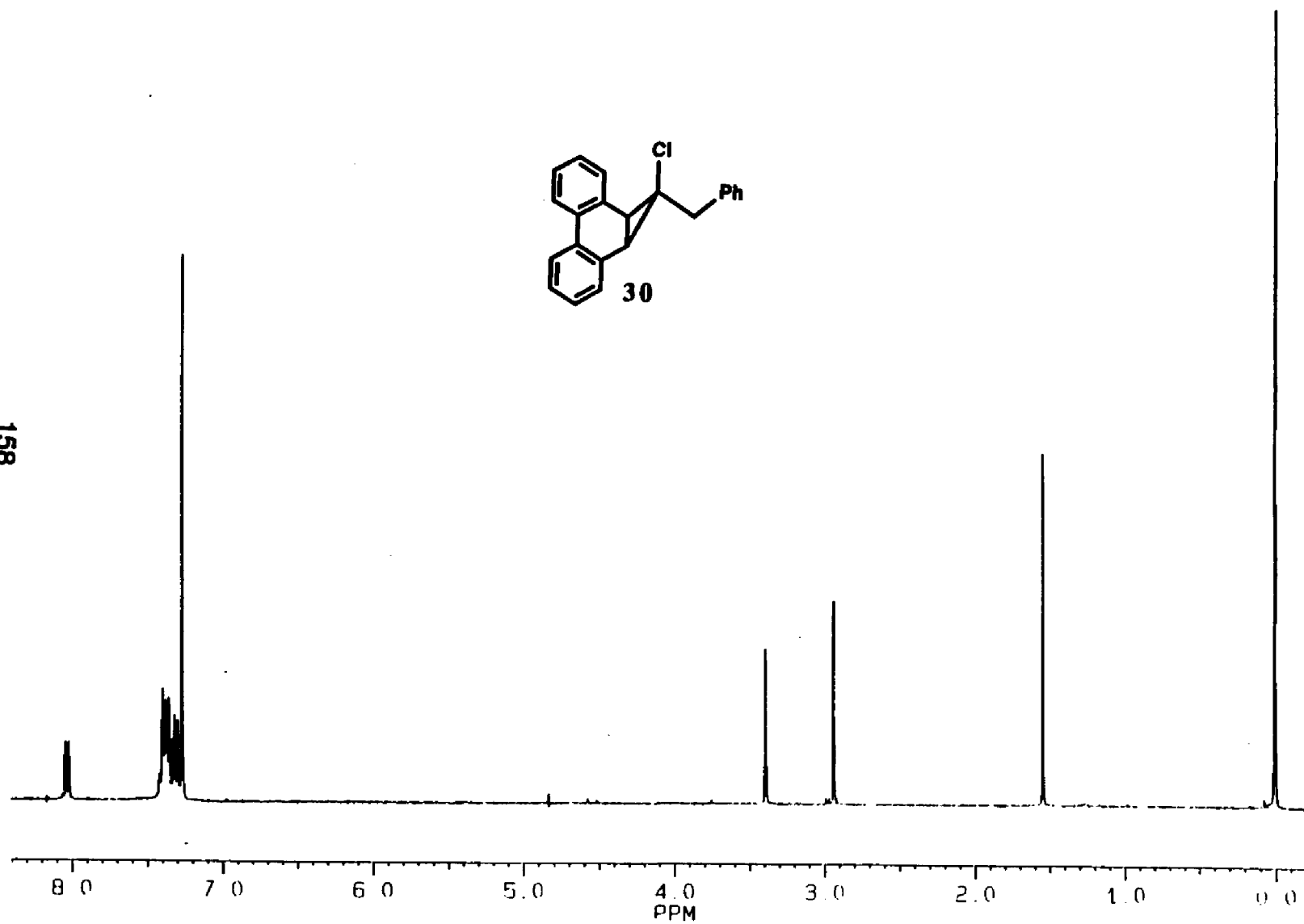
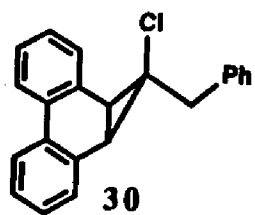




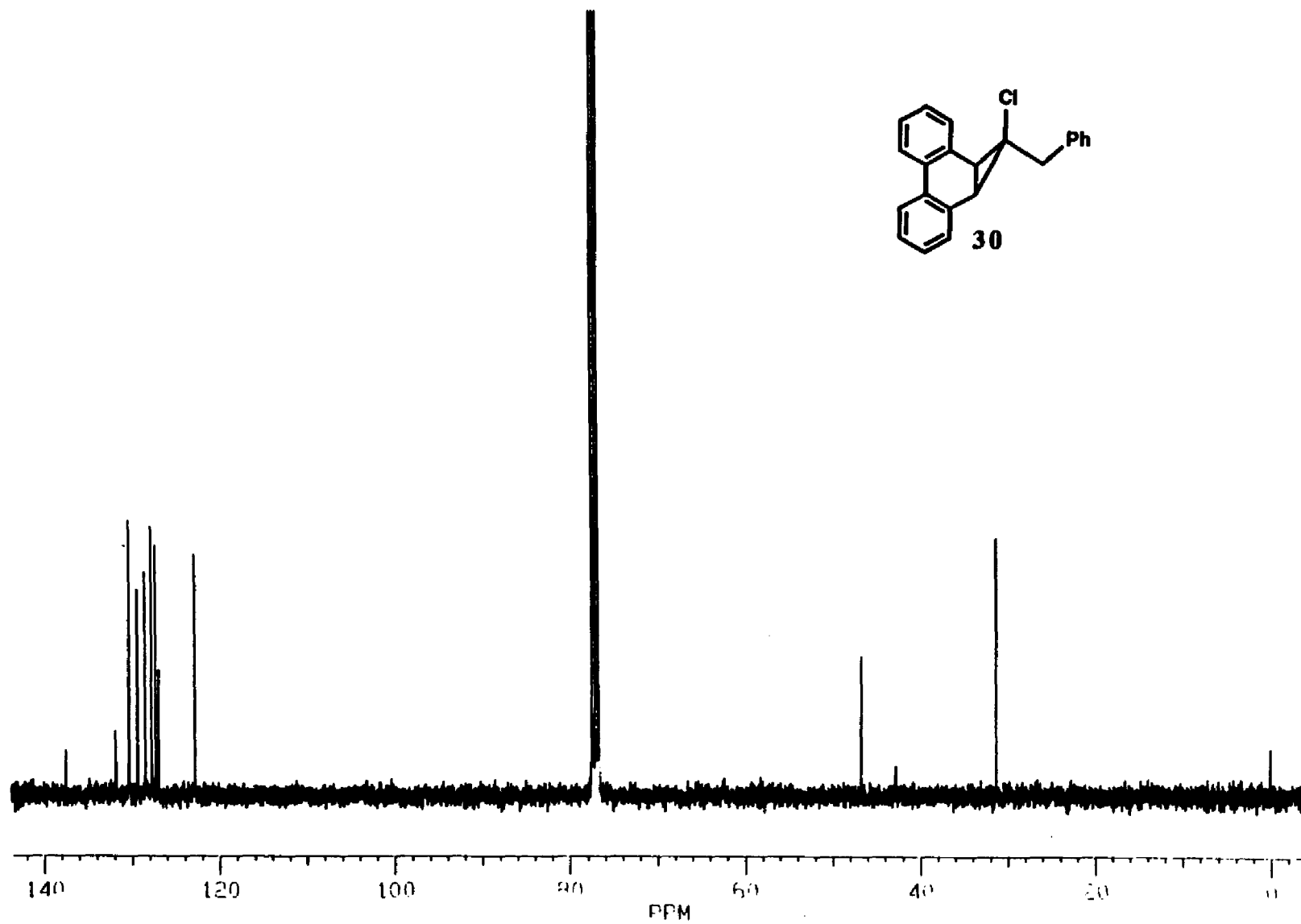


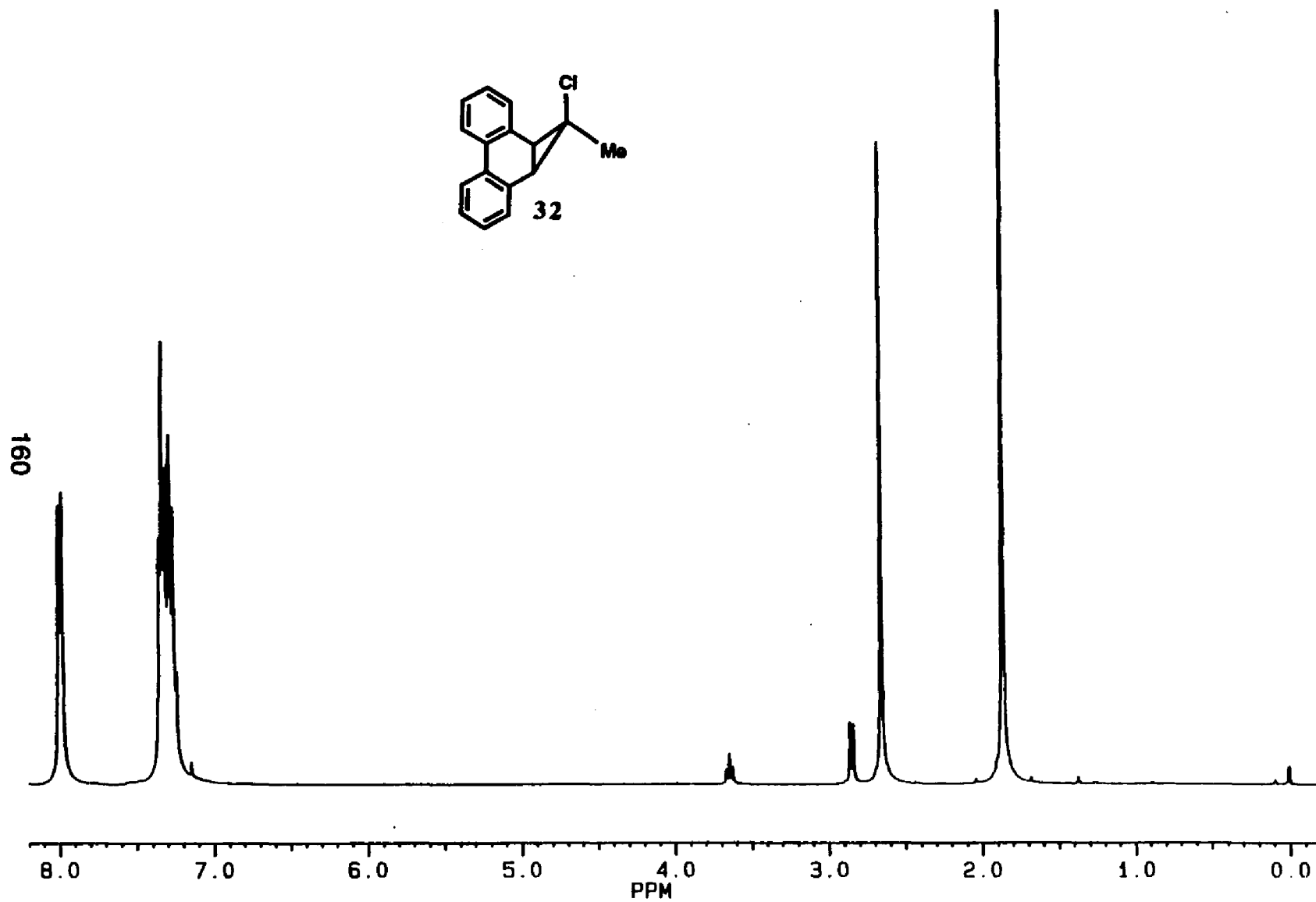
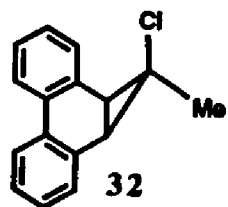


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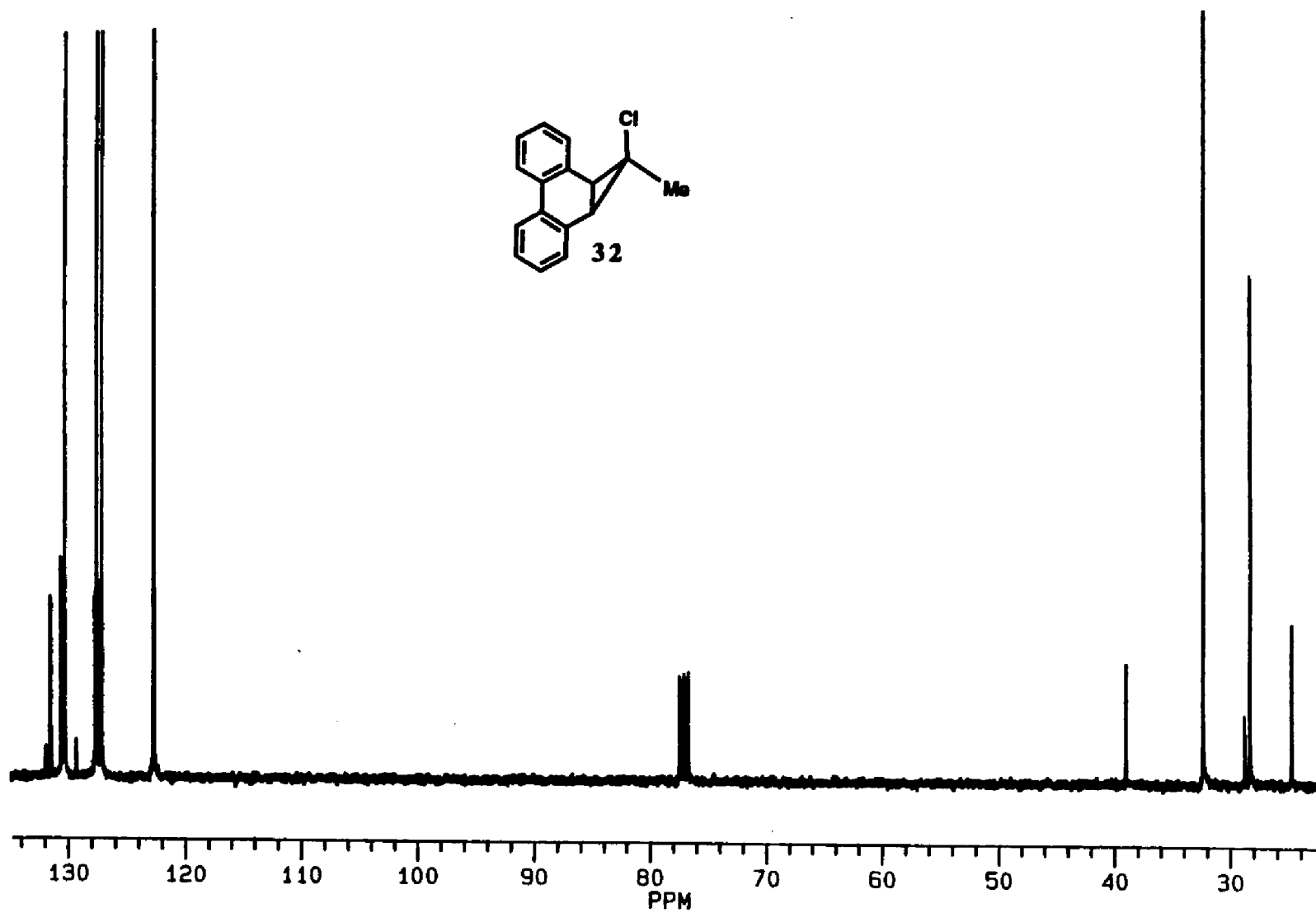


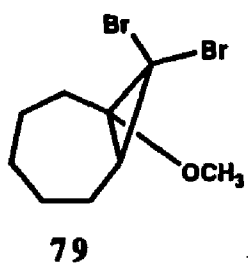
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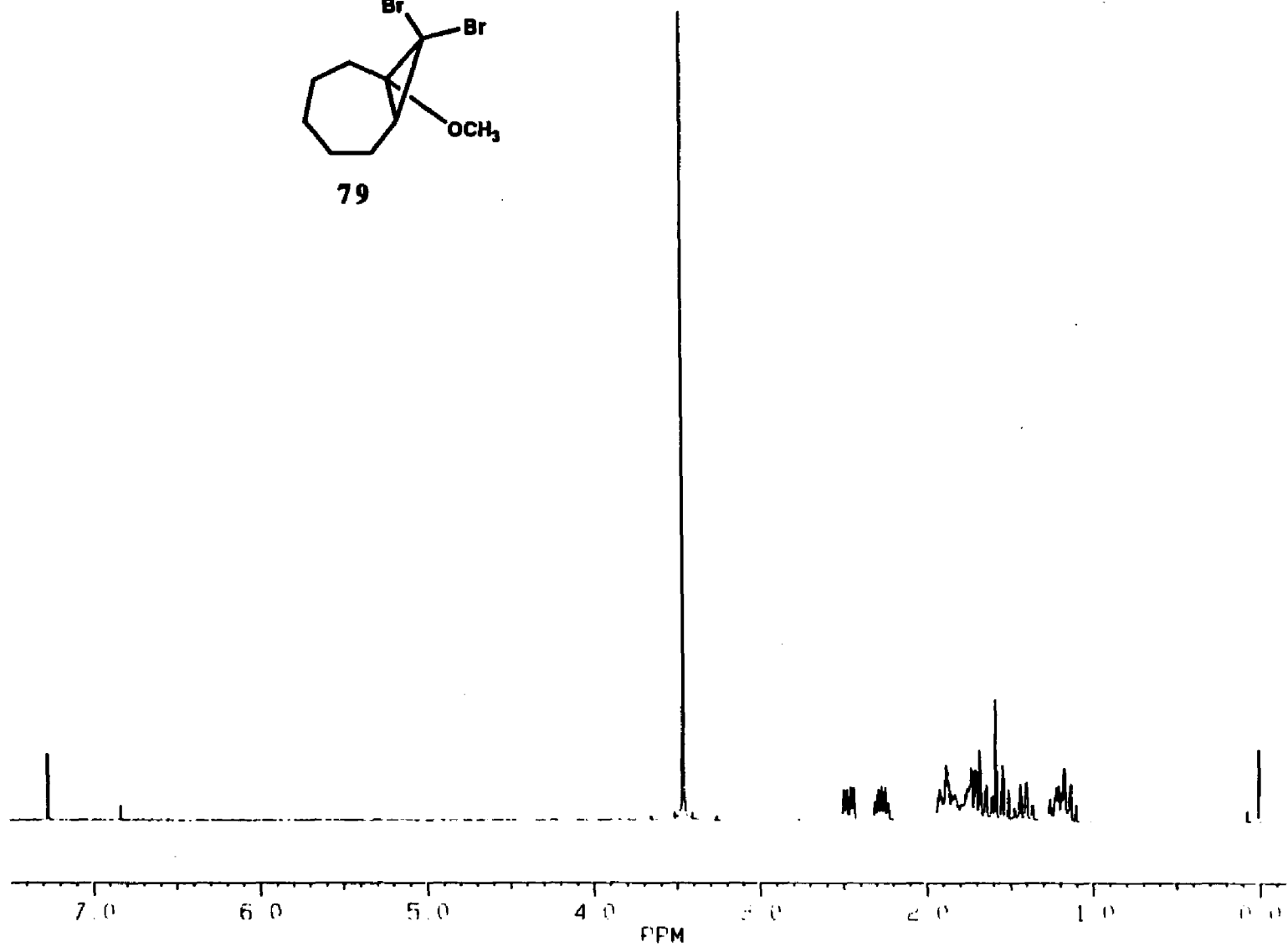


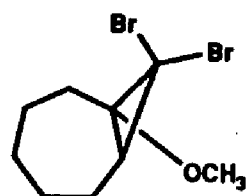
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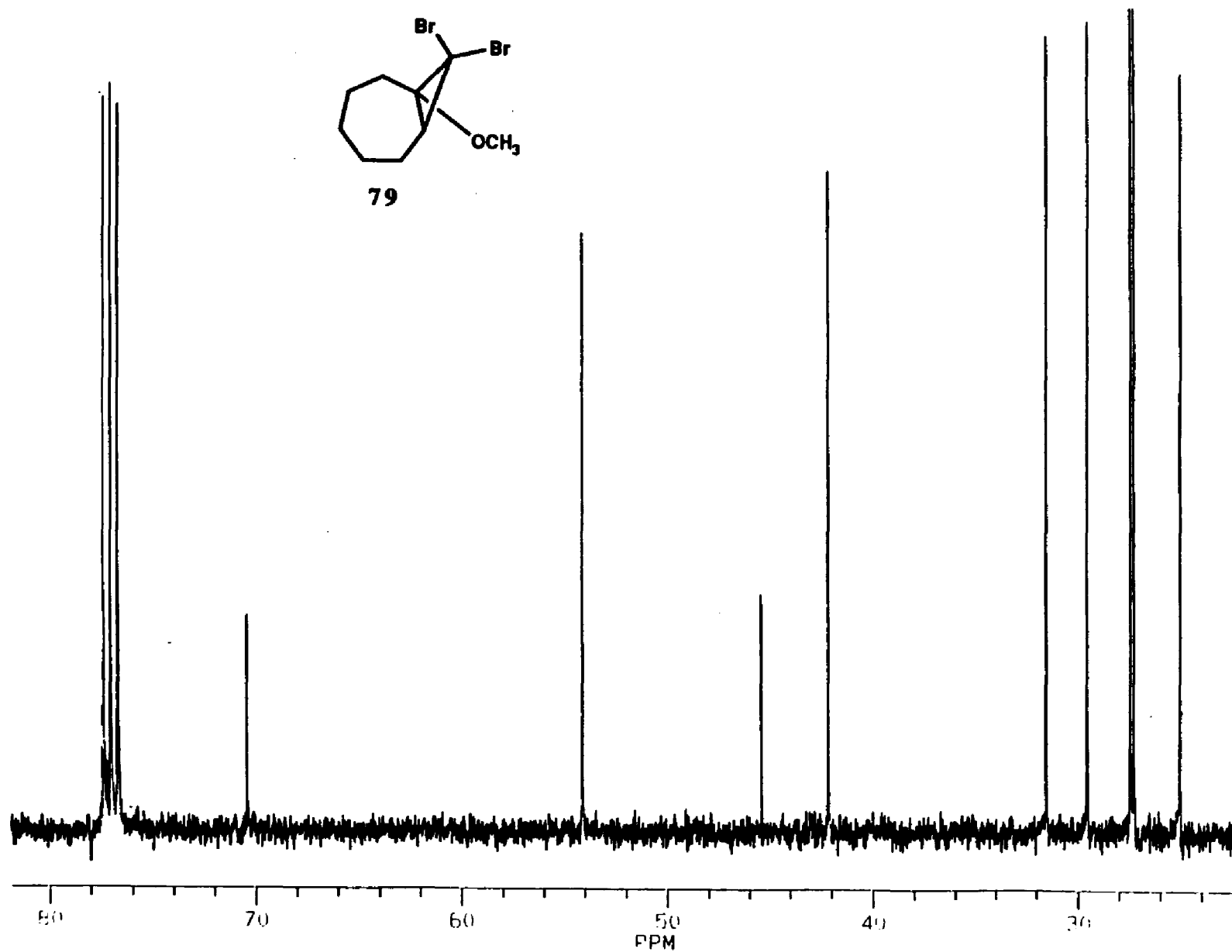
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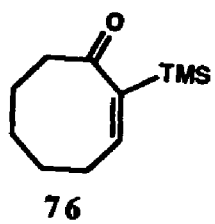


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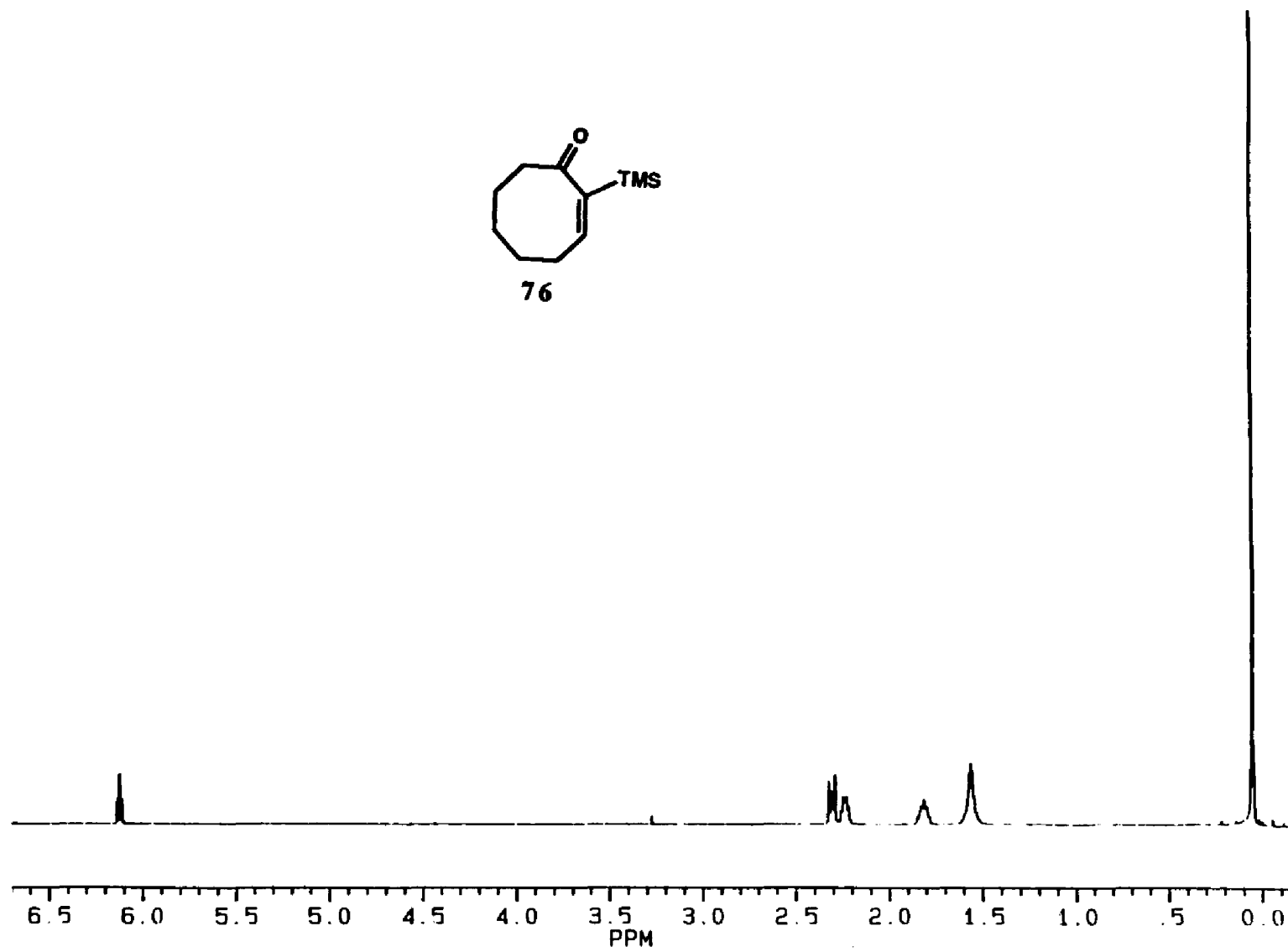
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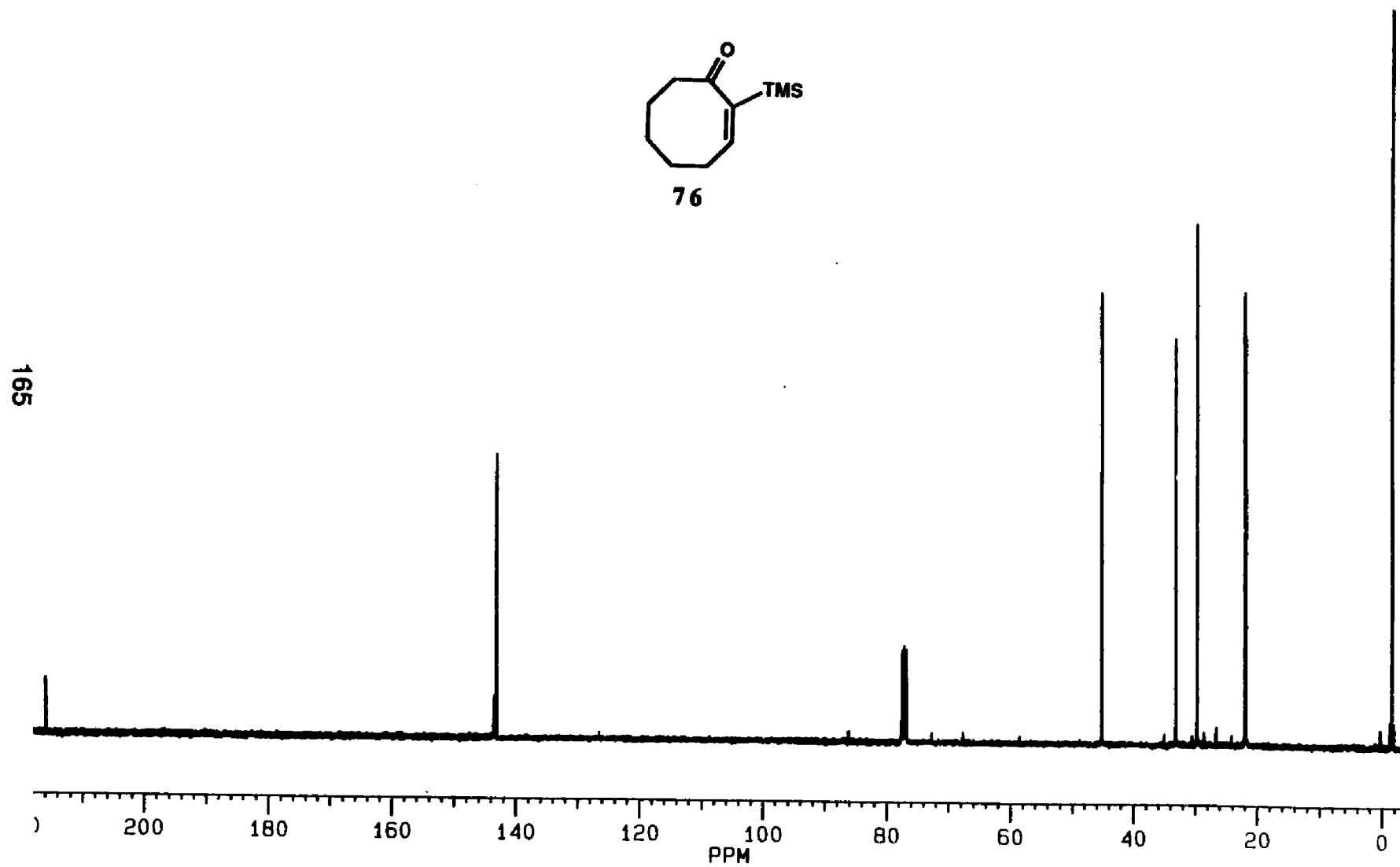
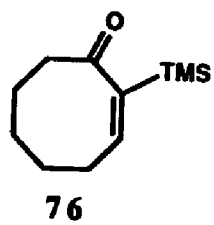




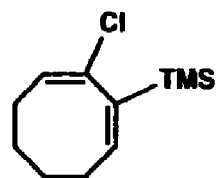


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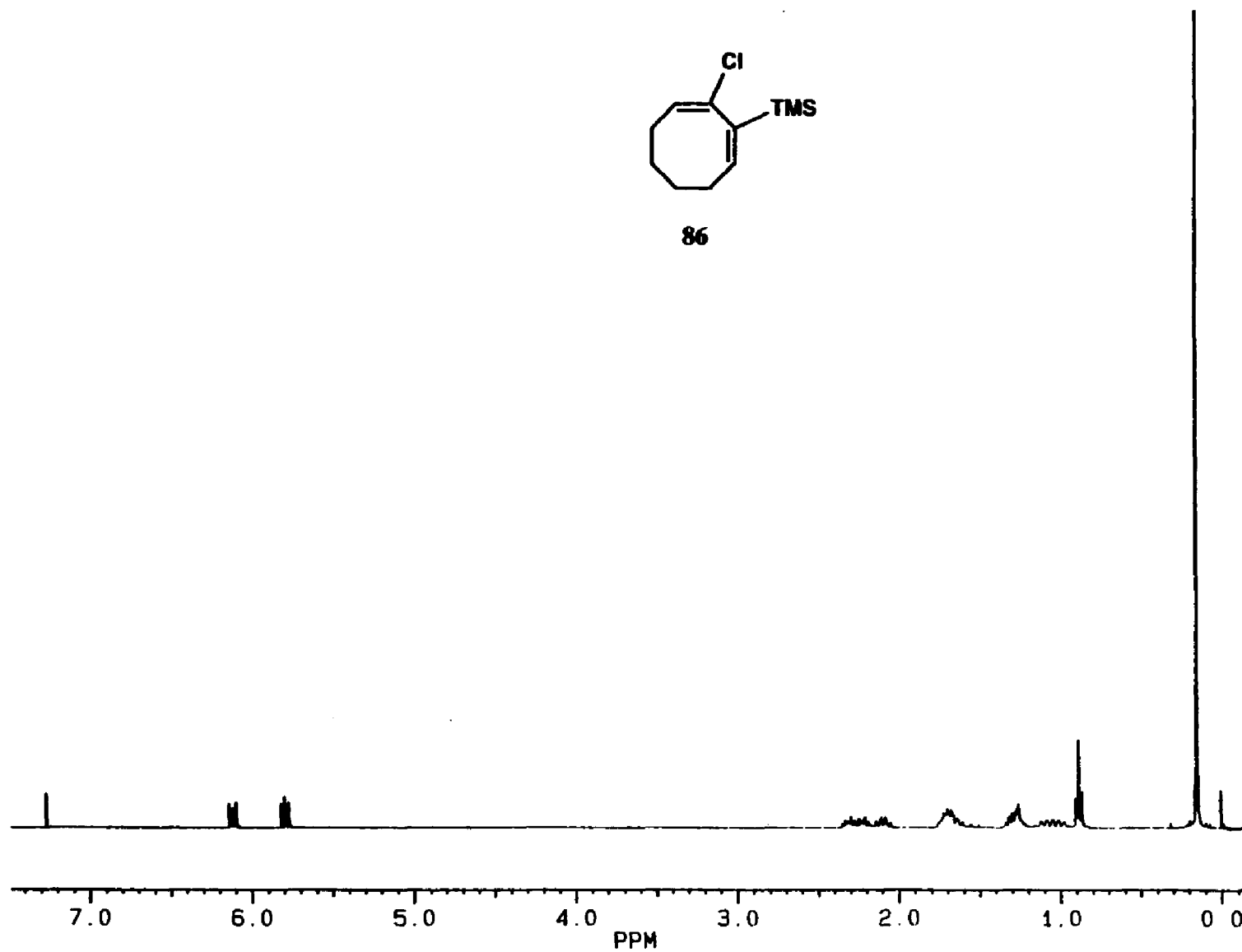


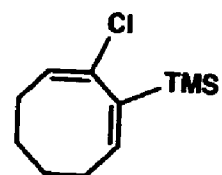


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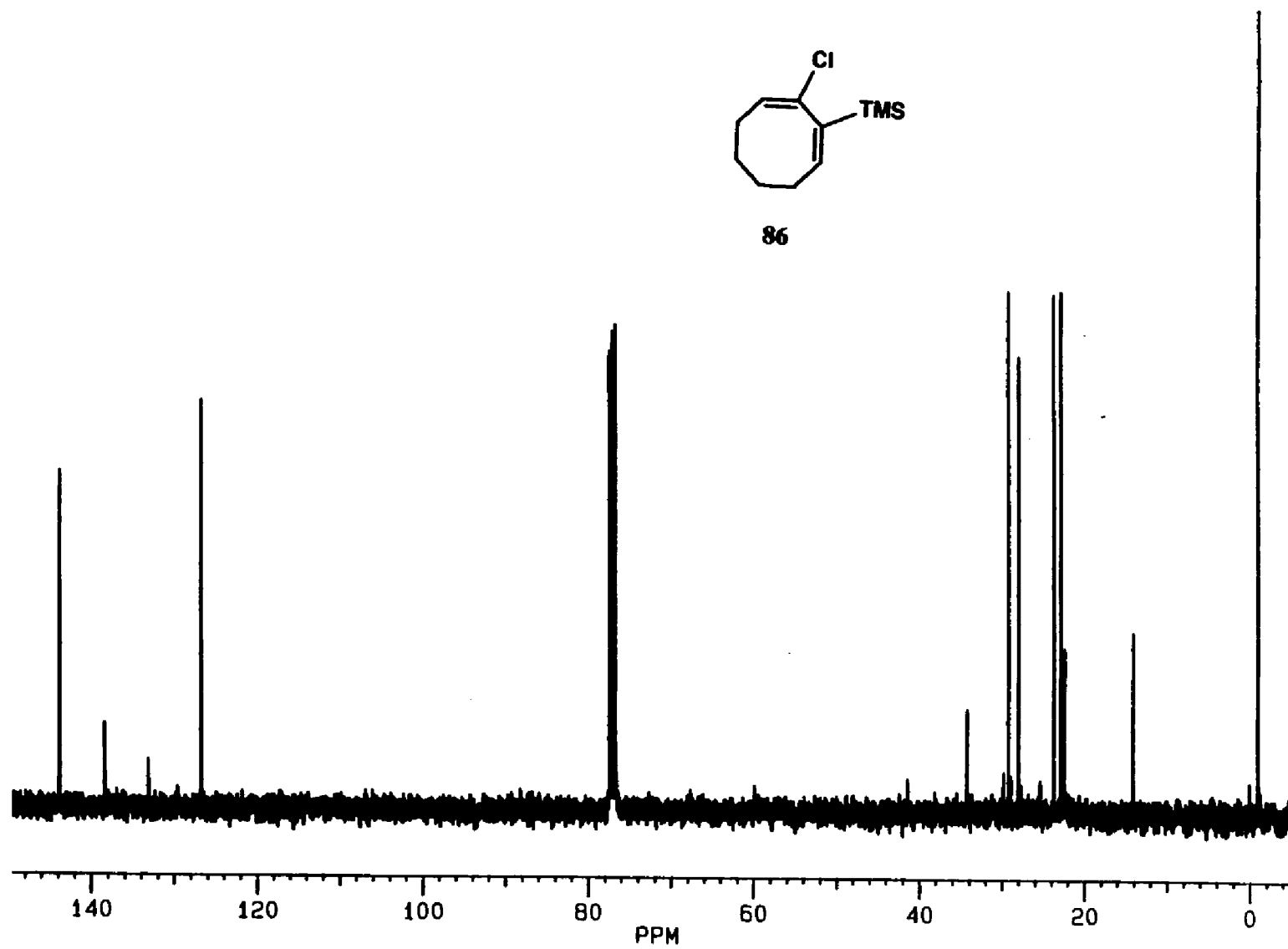
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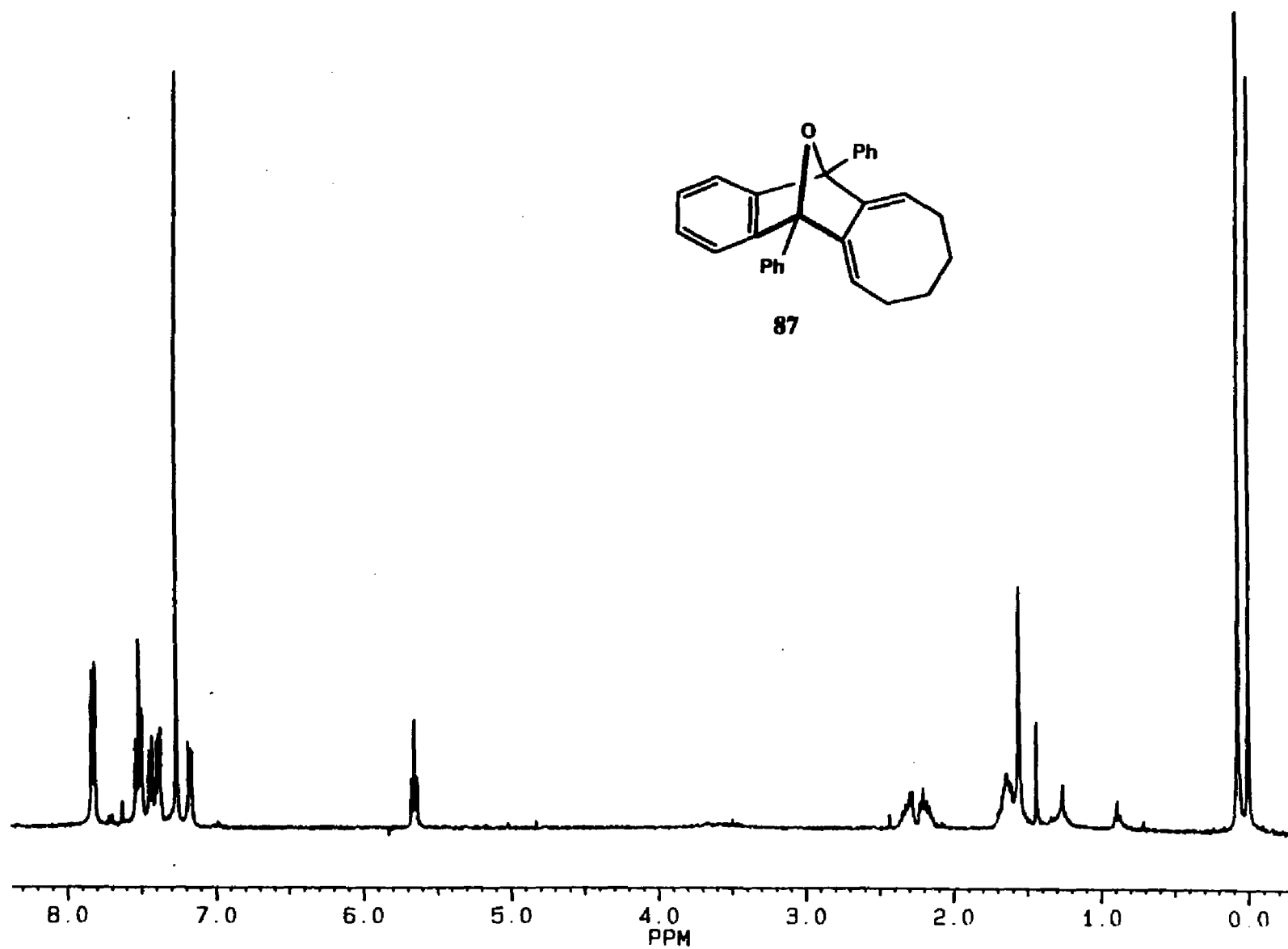


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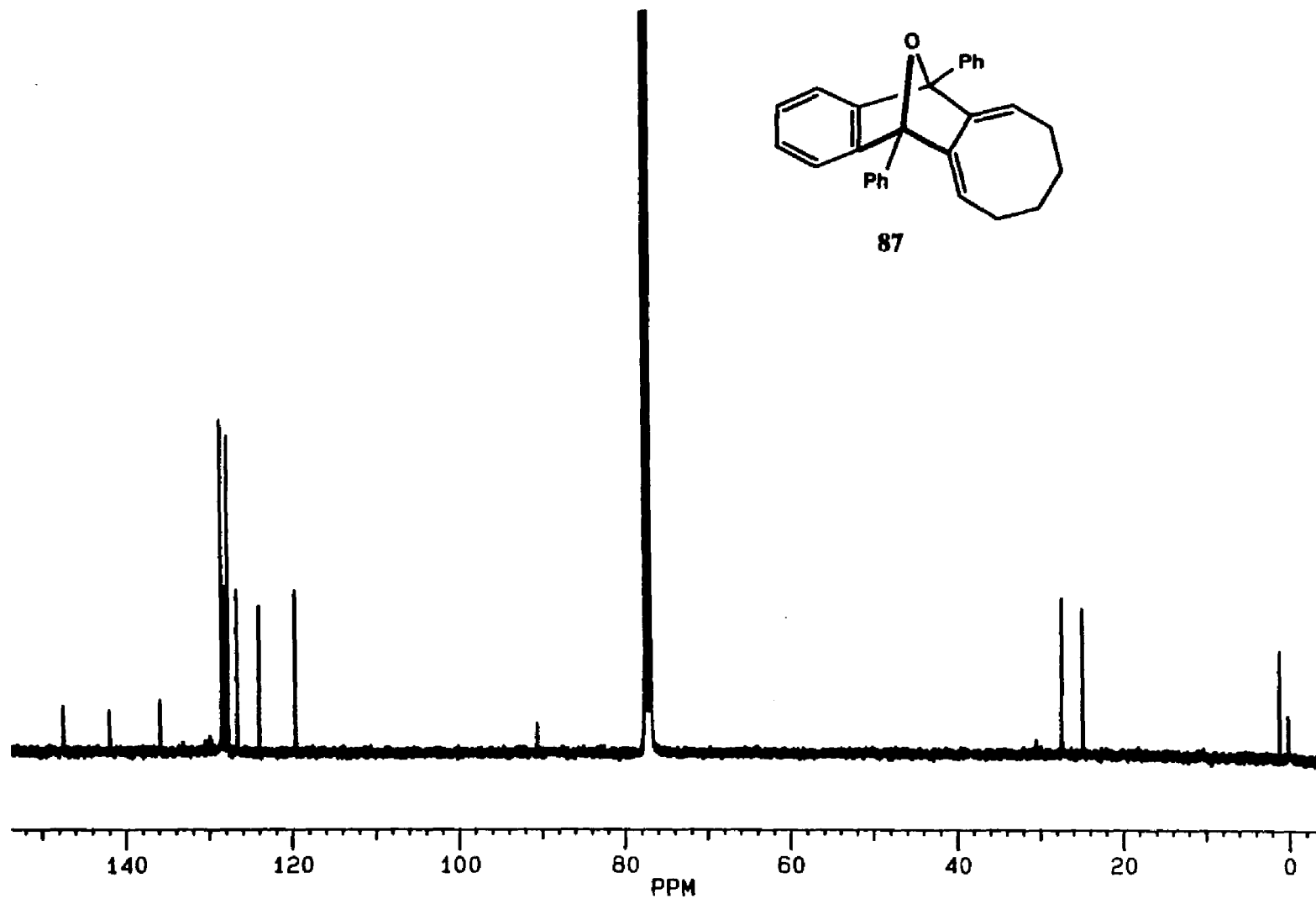
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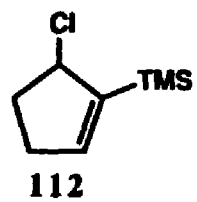


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